iranchembook.ir/edu

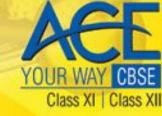
Advanced Chemistry Bloc

H2O

Chemistry Musing

You Ask ? We Answer 🗸





 O_2

CHEMISTRY teday

Volume 24

December 2015

Managing Editor Mahabir Singh Editor Anil Ahlawat (BE, MBA)

ONTENT

Corporate Office: Plot 99, Sector 44 Institutional area, Gurgaon -122 003 (HR).

Tel: 0124-4951200 e-mail: info@mtg.in website: www.mtg.in Read, Office:

No. 12

406, Taj Apartment, Near Safdarjung Hospital, New Delhi - 110029.

- **Chemistry Musing Problem Set 29** 8
 - **Practice Paper PMT Class XI** 12
 - Ace Your Way CBSE XI 17
 - **Examiner's Mind Class XI** 24
 - JEE Accelerated Learning Series 31
 - **Concept Map** 46
 - Ace Your Way CBSE XII 59
 - **Examiner's Mind Class XII** 68
 - **Advanced Chemistry Bloc** 78
- **Chemistry Musing Solution Set 28** 82
 - You Ask, We Answer 84
 - Crossword 85

Subscribe online at WWW.mtg.in

				abscribe (mine at		
Individual Subscription Rates			Combined Subscription Rates				
	1 yr.	2 yrs.	3 yrs.		1 yr.	2 yrs.	3 yrs.
Mathematics Today	330	600	775	PCM	900	1500	1900
Chemistry Today	330	600	775	РСВ	900	1500	1900
Physics For You	330	600	775	PCMB	1000	1800	2300
Biology Today	330	600	775				

Send D.D/M.O in favour of MTG Learning Media (P) Ltd.

Payments should be made directly to : MTG Learning Media (P) Ltd, Plot No. 99, Sector 44, Gurgaon - 122003 (Haryana) We have not appointed any subscription agent.

Owned, Printed and Published by Mahabir Singh from 406, Taj Apartment, New Delhi - 29 and printed by Personal Graphics and Advertisers (P) Ltd., Okhla Industrial Area, Phase-II, New Delhi. Readers are adviced to make appropriate thorough enquiries before acting upon any advertisements published in this magazine. Focus/Infocus features are marketing incentives. MTG does not vouch or subscribe to the claims and representations made by advertisers. All disputes are subject to Delhi jurisdiction only. Editor : Anil Ahlawat

Copyright© MTG Learning Media (P) Ltd. All rights reserved. Reproduction in any form is prohibited.



CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 29

JEE MAIN/PMTs

- Ratio of the rates of diffusion of He and H₂ at 0°C is same to the case
 - (I) when temperature is changed to 100°C
 - (II) when O_2 and CH_4 are taken instead of He and H_2 respectively
 - (III) when volume of the flask is doubled
 - (IV) when CH_4 and O_2 are taken instead of He and H_2 respectively.
 - (a) I and II (b) II and III
 - (c) I, II and III (d) I and IV
- 2. Study the given sequence of reactions :

$$// + H_2 \xrightarrow{1, 4-addition} A \xrightarrow{O_3/H_2O/Zn} B$$
$$D \xleftarrow{Ca(OH)_2} C \xleftarrow{Oxidation}$$

If 'D' is an ozonolysis product of 'E' then 'E' is

$$\begin{array}{c|c} (a) & (b) \\ (c) & (d) \\ \end{array}$$

- **3.** Which reaction yields the greatest quantity of chlorine from a given quantity of hydrochloric acid?
 - (a) Warming conc. HCl with MnO_2
 - (b) Warming conc. HCl with Pb₃O₄
 - (c) Mixing conc. HCl with $KMnO_4$
 - (d) Treating bleaching powder with HCl
- **4.** A weak monobasic acid is titrated against NaOH. After the addition of 20 mL and 40 mL of NaOH the

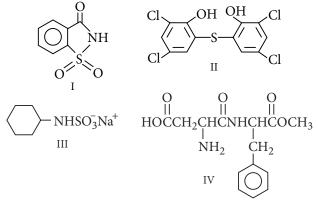
CHEMISTRY TODAY | DECEMBER '15

pH of solutions are 4 and 5 respectively. The volume of NaOH required to reach equivalence point is

- (a) 35 mL (b) 3.5 mL
- (c) 45 mL (d) 40 mL
- 5. Study the given sequence of reactions,
 - A + NaOH $\xrightarrow{\Delta} B \xrightarrow{\text{HCl}}$ White fumes
 - $\xrightarrow[White ppt]{CaCl_2} C \xrightarrow[White ppt]{KMnO_4(acid)} Colourless$
 - A, B and C are respectively
 - (a) Al_2O_3 , NH_3 and $H_2C_2O_4$
 - (b) $(NH_4)_2C_2O_4$, NH₃ and CaC₂O₄
 - (c) NH_4OH , $H_2C_2O_4$, CaC_2O_4
 - (d) none of these.

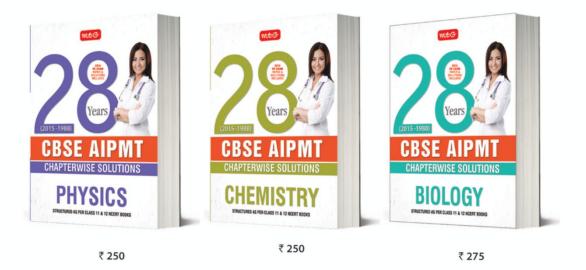
JEE ADVANCED

6. Consider the following synthetic compounds :



Which of the above compounds are used as sweetening agents?

The most comprehensive question bank books that you cannot afford to ignore



28 Years' Physics, Chemistry & Biology contain not only chapterwise questions that have appeared over the last 28 years in CBSE's PMT, but also full solutions, that too by experts. Needless to say, these question banks are essential for any student to compete successfully in AIPMT. More so since almost 50% of questions in AIPMT are from previous years.

HIGHLIGHTS:

- Chapterwise questions of last 28 years' (2015-1988) of CBSE-PMT
- Chapterwise segregation of questions to help you assess the level of effort required to succeed
- An unmatched question bank series with close to 1,000 pages having detailed solutions by experts



Scan now with your smartphone or tablet*

Visit www.mtg.in for latest offers and to buy online!



Available at all leading book shops throughout the country. For more information or for help in placing your order: Call 0124-4951200 or email info@mtg.in

*Application to read QR codes required

(a) I, III and IV	(b) II, III and IV
(c) I, II and IV	(d) All of these

COMPREHENSION

Faraday's first law of electrolysis : The mass of a substance liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte. Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb.

Faraday's second law of electrolysis: When the same quantity of electricity is passed through different electrolytes connected in series, the masses of the substances produced at the electrodes are directly proportional to their equivalent weights.

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

The volume of gases evolved by passing 0.965 A current for 1 hour through an aqueous solution of CH₃COONa at 25°C and 1 atm is

(a) 2.762 L	(b) 1.762 L
(c) 17.62 L	(d) none of these.

If three faradays of electricity is passed through the solutions of AgNO₃, CuSO₄ and AuCl₃, the molar ratio of the cations deposited at the cathode is
(a) 1:1:1
(b) 1:2:3

(c) 3:2:1 (d) 6:3:2

INTEGER VALUE

- 9. Number of σ bonds present in the molecule of tetracyanoethylene is
- **10.** Histidine has pK_a values as indicated

$$\overset{6.04}{\overset{}}_{N}\overset{CH_2-CH-C-OH}{\overset{}}_{H}\overset{H}{\overset{}}_{9.17}$$

At pH = 8, the total number of nitrogen atoms which exist in protonated form is

۰

CBSE Scraps Problem Solving Assessment Test for Std. IX, XI

Mid-way through the academic year, the Central Board of Secondary Education (CBSE) on 30 October, 2015 decided to do away with the Problem Solving Assessment (PSA) test from the 2015-2016 academic year. The assessment began in 2013 for students of classes IX and XI, who were expected to solve application-based problems to hone their research and analytical skills.

Ever since the PSA was introduced, it was resented by faculty members and students, who cited its ambiguous nature of the assessment, particularly students inclined towards humanities and social sciences subjects. The test aimed to help students assess their ability to comprehend and process information and did not merely assess the subject matter.

On 30 October, 2015 afternoon, to the surprise of CBSE school principals, an e-mail came from the regional office, intimating them of the PSA being dropped with immediate effect. K.K. Choudhury, Controller of Examination, in his communication to school principals, said

that the board has "decided to do away with the conduct of PSA in classes IX and XI from the session 2015-2016".

Students who were unable to attend the PSA in class IX and scored poor marks were allowed to take up a formative assessment test in class X. 30 October, 2015 circular issued by the board, however, asks school to conduct a formative assessment for students who were in class IX in 2014-2015 academic year and could not attend the PSA or want to improve their scores.

While a section of teachers welcomed the move, saying that there was a lot of "ambiguity" and it was a hard assessment to crack, a teacher of the Bengaluru-based school, however, said that this was a "good experiment" of the board that failed since it did not have clear cut directions.

Deepa Sridhar, principal, Sri Kumaran's Children's Home, Bengaluru, said that she was not happy with the move as she felt that it was a good method for students to analyse their aptitude. "Particularly in the light of emphasis given to the Continuous and Comprehensive Evaluation method, assessments like the PSA would help children as well as us gauge their aptitude," she said.

What PSA is all about

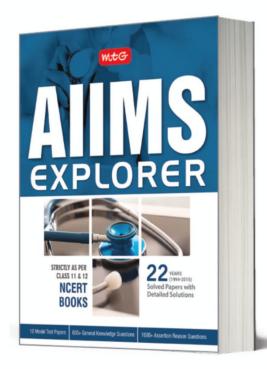
One of the objectives of the assessment was to help students analyse life situations, comprehend and interpret it. The test assesses three aspects such as language convention, qualitative reasoning and quantitative reasoning. Problem Solving Assessment (PSA) score is 10 per cent of total assessment for class IX for one language, mathematics, science and social science for class IX students. In class IX. students had three formative assessment, one PSA and two summative assessment. For class XI, students were issued separate certificate for the assessment. Once the students go to class X and XII (who appeared for PSA when they were in IX and XI) they are given the option to improve their PSA score. It consists of 60 multiple choice questions that carry 60 marks.

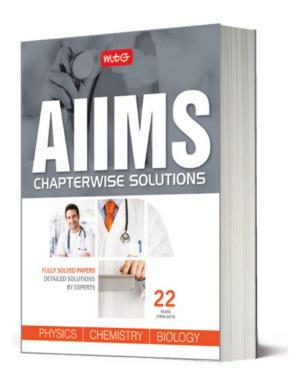
Courtesy : The Hindu





The most Reliable and Featured 22 Years' AIIMS EXPLORER and AIIMS CHAPTERWISE SOLUTIONS in the market





• 22 years' (1994-2015) Chapterwise Solutions

· Subjectwise distribution of 22 years' questions

HIGHLIGHTS:

- 22 years' (1994-2015) Solved Papers with Detailed Solutions
- 10 Model Test Papers
- 600+ General Knowledge Questions
- 1600+ Assertion Reason Questions



Available at all leading book shops throughout the country. For more information or for help in placing your order: Call 0124-4951200 or email:info@mtg.in Visit www.mtg.in for latest offers and to buy online!



SINGLE OPTION CORRECT

This paper contains 45 **multiple choice questions**. Each question has four choices (a), (b), (c) and (d), out of which **ONLY ONE** is correct. (Mark only One Choice).

Marks : 45×4=180

- The total spin resulting from a d⁷ configuration is

 (a) 3/2
 (b) 1/2
 (c) 2
 (d) 1
- 2. A certain particle carries 2.5×10^{-16} C of static electric charge. Calculate the number of electrons present in it.
 - (a) 1563 (b) 15630
 - (c) 3021 (d) 2345
- **3.** The quantum numbers of four electrons are given below :

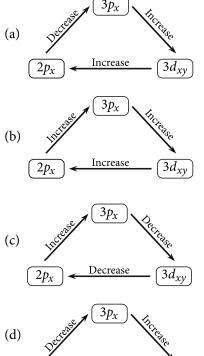
		n	1	m	\$
(1) Ele	ctron 1	3	0	0	-1/2
(2) Ele	ctron 2	4	0	1	1/2
(3) Ele	ctron 3	3	2	0	1/2
(4) Ele	ctron 4	3	1	0	-1/2

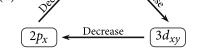
The correct order of decreasing energy of these electrons is

- (a) Electron 3>Electron 1>Electron 4>Electron 2
- (b) Electron 4>Electron 2>Electron 1
- (c) Electron 3>Electron 2>Electron 1
- (d) Electron 2>Electron 4>Electron 3 >Electron 1
- 4. $\frac{1}{4}$ th of Avogadro number of atoms of an element

absorb energy 'X' kJ for ionisation, the ionisation energy of one atom of the element is







6. The following subshells are involved for 6th period elements in periodic table except

(a) 4 <i>f</i>	(b) 5 <i>d</i>
(c) 6 <i>s</i>	(d) 5 <i>p</i>

Contributed by Dr. Sangeeta Khanna, Chemistry Coaching Circle, Chandigarh, 09814129205

Negative Marking (-1)

5. Which of the following is correct about energy?

7. From the given set of species, point out the species from each set having the least atomic radius :

(P) O^{2-} , F⁻, Na⁺ (Q) Cu, Zn, Na (R) Li, Be, Mg (S) He, Li⁺, H⁻ Correct answer is (a) O^{2-} , Cu, Li, H⁻ (b) Na⁺, Cu, Be, Li⁺

- (c) F^{-} , Zn, Mg, He (d) Na⁺, Cu, Be, He
- **8.** In the reaction,

 $2H_2O_2 \longrightarrow 2H_2O + O_2$

- (a) oxygen is oxidised only
- (b) oxygen is reduced only
- (c) oxygen is neither oxidised nor reduced
- (d) oxygen is both oxidised and reduced.
- 9. What is the maximum number of orbitals that can be identified with the following quantum number n = 3, l = 1, m_l = 0 ?
 (a) 4 (b) 1 (c) 2 (d) 3
- **10.** In the given reaction,

 $K_2Cr_2O_7 + X H_2SO_4 + Y SO_2 \longrightarrow K_2SO_4$ $+ Cr_2(SO_4) + Z H_2O$ X, Y, Z are

- (a) 1, 3, 1 (b) 4, 1, 4 (c) 3, 2, 3 (d) 2, 1, 2
- 11. 20 cm³ of a gaseous hydrocarbon was mixed with 150 cm^3 of oxygen. The mixture was sparked so that the hydrocarbon was completely burnt. The gaseous products had a total volume of 130 cm^3 . When this product was passed over soda lime, the volume of the product decreases to 90 cm³. All gases were measured at S.T.P. Deduce the molecular formula of the hydrocarbon.

(a) C_2H_4 (b) CH_4 (c) C_2H_2 (d) C_2H_6

- 12. In which one of the following pairs of the species are isoelectronic as well as isotopic? (At. no. of Ca = 20, Ar = 18, K = 19, Mg = 12, Fe = 26, Na = 11) (a) ${}^{40}Ca^{+2}$, ${}^{40}Ar$ (b) ${}^{39}K^+$, ${}^{40}K^+$ (c) ${}^{24}Mg^{+2}$, ${}^{25}Mg$ (d) ${}^{23}Na$, ${}^{24}Na^+$
- **13.** Which of the following contains maximum number of particles?
 - (a) 1 kg electron
 - (b) 10^5 mg neutron
 - (c) 1 kg proton
 - (d) 1000 g hydrogen atom
- **14.** Identify the incorrect statement(s).
 - I. The maximum probability of finding electron in the $d_{x^2-y^2}$ orbital is at an angle of 45° from *x* and *y*-axes.
 - II. Each *f*-orbital has a total of four nodes.

- III. At same velocity a neutron has lesser wave nature than an electron.
- (a) I and II (b) II and III
- (c) I and III (d) All of these
- 15. Reason of lanthanoid contraction is(a) decreasing screening effect
 - (b) negligible screening effect of 'f' orbitals
 - (c) increasing nuclear charge
 - (d) decreasing nuclear charge.
- **16.** For a hydrogen atom, which electronic transition would result in the emission of a photon with the highest energy?
 - (a) $5f \longrightarrow 3d$ (b) $4p \longrightarrow 2s$
 - (c) $3p \longrightarrow 6d$ (d) $2s \longrightarrow 3p$
- 17. The masses of photons corresponding to the first lines of the Lyman and the Balmer series of the atomic spectrum of hydrogen are in the ratio of (a) 4:9 (b) 27:5 (c) 9:4 (d) 1:1
- 18. 0.25 g of an element '*M*' react with excess of fluorine to produce 0.547 g of MF_6 . Approximate atomic mass of *M* is [At. mass of F = 19] (a) 52 (b) 95 (c) 32 (d) 206
- 19. A metallic oxide contains 40% oxygen. How many electrons will be present in valence shell of metal if its atomic mass is 24?
 (a) 3 (b) 2 (c) 1 (d) 4
- **20.** What will be the four quantum numbers of last electron of Sc 21?
 - (a) $n = 4; l = 0; m = 0, s = +\frac{1}{2}$ (b) $n = 3; l = 2; m = 0; s = +\frac{1}{2}$ (c) $n = 4; l = 1; m = 0; s = +\frac{1}{2}$ (d) $n = 3; l = 3; m = 0; s = +\frac{1}{2}$
- **21.** The angular momentum of 3*p*-orbitals in terms of $\hbar \left\{ \hbar = \frac{h}{2\pi} \right\}$ is

(a)
$$\sqrt{2\hbar}$$
 (b) $2\hbar$
(c) $\frac{\hbar}{\sqrt{2}}$ (d) $\frac{\hbar}{2\pi}$

22. How many of the following will have four unpaired electrons? [At. no. : Co = 27; Fe = 26; Sc = 21; Cu = 29; Cr = 24; Mn = 25]

CHEMISTRY TODAY | DECEMBER '15

B

- 23. The atomic masses of He and Ne are 4 and 20 a.m.u respectively. The value of the de Broglie wavelength of He gas at 200 K is 'M' times that of the de Broglie wavelength of Ne at 1000 K. 'M' is (a) 5 (b) 4 (c) 3 (d) 2
- 24. The atomic numbers of elements *X*, *Y*, *Z* are 19, 21 and 25 respectively. The number of electrons present in the 'M' shells of these elements follow the order

(a) Z > Y > X(b) X > Y > Z

(c) Z > X > Y(d) Y > Z > X

25. Which of the following statements is correct?

- (a) Oxidation state of carbon in C_3O_2 is $+\frac{2}{3}$.
- (b) Oxidation state of oxygen in ozone is -2.
- (c) Oxidation state of oxygen in potassium superoxide is $+\frac{1}{2}$
- (d) Oxidation states of nitrogen in ammonium nitrate are -3 and +5.
- 26. In which of the following changes both the electrons are removed from same orbital?
 - (a) Cu \longrightarrow Cu²⁺ + 2e⁻
 - (b) $Cr \longrightarrow Cr^{2+} + 2e^{-}$
 - (c) Ge \longrightarrow Ge²⁺ + 2e⁻ (d) Zn \longrightarrow Zn²⁺ + 2e⁻
- 27. The chemistry of lithium is very similar to that of magnesium even though they are placed in different groups. Its reason is that
 - (a) both are found together in nature
 - (b) both have nearly the same size
 - (c) both have similar electronic configuration
 - (d) the ratio of their charge to size is nearly the same.
- 28. Which of the following does not have three significant figures?
 - (a) 6.02×10^{23} (b) 0.25
 - (c) 6.60×10^{-34} (d) 1.50
- 29. In which of the following first ion or element is less electronegative? .2

(a)	F and Cl	(b)	Fe ⁺³	and Fe ⁺²
(c)	O and N	(d)	S an	d N

30. Which of the following elements will have highest 3rd ionisation energy?

(c) Fe (a) Be (b) Mg (d) Mn

- **31.** Electron affinity of 2nd period element is less than 3^{rd} period elements of *p*-Block due to
 - (a) less effective nuclear charge
 - (b) more repulsion between valence electron and added electron

(c) absence of *d*-orbitals is
$$2^{nd}$$
 shell

- (d) 2^{nd} period elements cannot expand their octet.
- 32. Which of the following is correct order of conductance of ions in aqueous solution?
 - (a) $\text{Li}_{(aq.)}^+ > \text{Na}_{(aq.)}^+ > \text{K}_{(aq.)}^+ > \text{Rb}_{(aq.)}^+ > \text{Cs}_{(aq.)}^+$
 - (b) $\text{Li}_{(aq.)}^+ < \text{Na}_{(aq.)}^+ < \text{K}_{(aq.)}^+ < \text{Rb}_{(aq.)}^+ < \text{Cs}_{(aq.)}^+$
 - (c) $\text{Li}_{(aq.)}^+ < \text{K}_{(aq.)}^+ < \text{Na}_{(aq.)}^+ < \text{Rb}_{(aq.)}^+ < \text{Cs}_{(aq.)}^+$
 - (d) None of these
- 33. Which of the following elements has three outermost incomplete shells?
 - (b) I (53) (a) Kr (36)

(d) Ga (31) (c) La (57)

- 34. A non-radioactive element is paramagnetic and also form coloured paramagnetic compounds which can act as a catalyst. This element will be placed preferably in which block of periodic table? (a) s-Block (b) *p*-Block
 - (d) f-Block (c) *d*-Block
- 35. Which of the following compounds will have maximum covalent character?
 - (b) AgCl (c) AgI (d) AgBr (a) AgF
- 36. What is the mass of the precipitate formed when 8.45 g solution of AgNO₃ is mixed with 2.9 g NaCl solution? [Mol. wt. of AgNO₃ = 170; Mol. wt. of NaCl = 58.5; Mol. wt. of AgCl = 143.5] (a) 7 g (b) 14 g (c) 28 g (d) 3.5 g
- 37. What is the mole fraction of the solute in a 1.00 m aqueous solution ?
 - (a) 0.0354 (b) 0.0177 (c) 0.177 (d) 1.770
- 38. Which is the correct order of increasing energy of the listed orbitals in the atom of titanium? (At. no. Z = 22)
 - (a) 3s 3p 3d 4s (b) 3s 3p 4s 3d (c) 3s 4s 3p 3d (d) 4s 3s 3p 3d
- 39. 0.24 mol of a magnesium carbonate sample decomposes on heating to give carbon dioxide and 8.0 g magnesium oxide. What will be the percentage purity of magnesium carbonate in the sample? (At. wt. : Mg = 24)
 - (a) 60 (b) 83 (c) 75 (d) 96
- **40.** The number of water molecules is maximum in (a) 18 gram of water
 - (b) 18 moles of water
 - (c) 18 molecules of water
 - (d) 1.8 gram of water.



ASSERTION & REASON

In this type of questions, a statement of assertion (A) is followed by a statement of reason (R). Mark the correct choice as :

- (a) If A and R both are correct and R is the correct explanation of A.
- (b) If A and R both are correct but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.
- **41. Assertion :** The ψ_{640} represents an orbital. Reason : The orbital will be 6f.
- **42.** Assertion : Decomposition of CaCO₃ is an intramolecular redox reaction. Reason : Number of electrons lost by one element is equal to number of electrons gained by another of the same molecule in intramolecular redox.
- 43. Assertion : If specific heat of a metal is given, its approximate atomic mass can be calculated. Reason : According to Dulong and Petit's law, 6.4 approximate atomic mass of metal = Specific heat
- **44.** Assertion : α -rays possess maximum ionizing power. **Reason :** Kinetic energy of α -particles in α -rays is maximum among three types of radiations.
- **45.** Assertion : Fe^{2+} has 24 electrons hence, its electronic configuration is similar to that of $Cr(24): [Ar] 3d^{5}4s^{1}.$

Reason : All the five unpaired electrons in 3d gives stability to the ion.

SOLUTIONS

- **1.** (a): For d^7 , three unpaired electrons, $spin = 3 \times \frac{1}{2} = \frac{3}{2}$
- 2. (a): Charge on particle = 2.5×10^{-16} C

We know, charge on an electron = 1.6×10^{-19} C So, no. of electrons in the particle = $\frac{2.5 \times 10^{-16} \text{ C}}{1.6 \times 10^{-19} \text{ C}}$

- 3. (c): The correct order of decreasing energy will be: electron 3 which has higher energy than 2 and in the given order.
- 4. (b): $\frac{1}{4}N_0$ (*i.e.*, $\frac{1}{4}$ mole) atoms require energy = X kJ $1N_0$ (*i.e.*, 1 mole) atoms require energy = 4X kJ 1 atom requires energy = $\frac{4X}{N_0}$ kJ

5. (b)

8

- (d): 5p is filled in 5^{th} period.
 - **(b):** (P) $O^{2^-} > F^- > Na^+$ (Q) Cu < Zn < Na(R) Mg > Li > Be or Li > Be < Mg(S) H^- > He > Li⁺

8. (d) 9. (b)
10. (a):
$$6e^{-} + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

$$\frac{\left(SO_2 \longrightarrow SO_4^{2-} + 2e^{-}\right) \times 3}{2H^{+} + Cr_2O_7^{2-} + 3SO_2 \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O}$$

11. (a):
$$C_x H_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow x CO_2 + \frac{y}{2} H_2 O$$

20 20 $\left(x + \frac{y}{4}\right)$ 20 $x = 40$
 $x = 2$
Oxygen gas used = 150 - 90 = 60
20 $\left(2 + \frac{y}{4}\right) = 60 \Longrightarrow y = 4$

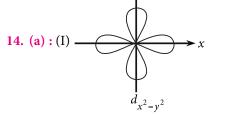
12. (b): The species which contain same number of electrons as well as same atomic number (Z), is known as isoelectronic and isotopic.

13. (a):

l

Number of electrons =
$$\frac{1}{9.1 \times 10^{-31}} = \frac{10^{31}}{9.1} = 1.1 \times 10^{30}$$

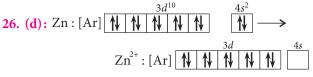
Number of protons = $\frac{1}{1.66 \times 10^{-24}} = 6.02 \times 10^{23}$
Number of neutrons = $\frac{10^5 \times 10^{-6}}{1.67 \times 10^{-24}} = 5.98 \times 10^{22}$
Number of H-atoms = $\frac{1000 \times 10^{-3}}{1.66 \times 10^{-24}} = 6.02 \times 10^{23}$



- (II) angular node = l and total node = n 1
- (III) due to more mass

15. (b) **16.** (b): 2 - 3 is absorption of energy 4 - 2 is emission of energy **17. (b)**: $\Delta E = mc^2$ For Lyman series, $m_1 c^2 \propto (1/1^2 - 1/2^2) \propto \frac{3}{4}$ For Balmer series, $m_2c^2 \propto (1/2^2 - 1/3^2) \propto \frac{5}{36}$ $m_1/m_2 = (3 \times 36)/(4 \times 5)$ $m_1: m_2 = 27: 5$ **18.** (b): $M + 3F_2 \longrightarrow MF_6$ Number of gram equivalents of M = Number of gram equivalents of MF_6 $\frac{0.25}{E} = \frac{0.547}{E+19}$ (where, E = Eq. weight of M) $E \times 0.25 + 4.75 = 0.547E$ $4.75 = 0.547E - 0.25E \Longrightarrow E = 15.8$ Eq. wt. \times valency = At. wt $15.8 \times 6 = At.$ wt. 94.8 = At. wt.**19.** (b): Eq. mass = 12; Valency $=\frac{24}{12}=2$ 20. (b) 21. (a): Angular momentum in an orbital $=\sqrt{\ell(\ell+1)}.\frac{h}{2\pi}$ $=\sqrt{1(1+1)}\cdot\frac{h}{2-}=\sqrt{2}\times\hbar$ **22.** (a) : Fe, Fe⁺², Mn⁺³, Cr⁺², Co⁺³ 23. (a): $\frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \sqrt{\frac{M_{\text{Ne}} K.E_{\text{Ne}}}{M_{\text{He}} \cdot K.E_{\text{He}}}} = \sqrt{\frac{M_{\text{Ne}} T_{\text{Ne}}}{M_{\text{He}} \cdot T_{\text{He}}}}$ $=\sqrt{\frac{20}{4} \times \frac{1000}{200}} = 5$

- 24. (a): As Z has 13 electrons, Y has 9 electrons and X has 8 electrons in M shell.
- 25. (d)



Both the electrons are removed from same orbital 4s.

27. (d): Similarity between Li and Mg is called diagonal similarity. Li⁺ and Mg²⁺ have similar ratio of charge to size (ϕ). 28. (b) 29. (d) 30. (a)

31. (b) 32. (b) 33. (c)

35. (c) 34. (c)

AgCl↓ + **36.** (a): AgNO₃ + NaCl \longrightarrow NaNO₃ Initial $\frac{8.45}{170}$ $\frac{2.9}{58.5}$ 0 = 0.049 mol = 0.049 mol After 0 0.049 mol 0.049 mol 0 reaction

Mass of AgCl precipitated = 0.049×143.5 g = 7 g

37. (b): 1.00 m solution means 1 mole solute is present in 1000 g water.

$$n_{\rm H_2O} = \frac{1000}{18} = 55.5 \text{ mol}$$

 $x_{\rm solute} = \frac{n_{\rm solute}}{n_{\rm solute} + n_{\rm H_2O}} = \frac{1}{1 + 55.5} = 0.0177$

- **38.** (b): Ti(22) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ Order of energy is 3s 3p 4s 3d
- **39.** (b): MgCO_{3(s)} \longrightarrow MgO_(s) + CO_{2(g)} Moles of $MgCO_3 = 0.24$ mol From above equation, 1 mole MgCO₃ gives 1 mole MgO
 - ... 0.24 mole MgCO₃ will give 0.24 mole MgO $= 0.24 \times 40 \text{ g} = 9.60 \text{ g MgO}$

:. % purity =
$$\frac{8}{9.6} \times 100 = 83\%$$

- **40. (b):** 1 mole water = 6.02×10^{23} molecules
 - \therefore 18 moles water = $18 \times 6.02 \times 10^{23}$ molecules

so, 18 moles water has maximum number of molecules.

- **41.** (c) : ψ represents an orbital. ψ_{640} means n = 6, l = 4, m = 0, i.e., 6g orbital.
- 42. (d)
- 43. (a): Both statements are correct because atomic mass of metal = $\frac{1}{\text{specific heat of metal}}$

۵ 🗞

44. (a)

45. (d)





CHAPTERWISE UNIT TEST : ORGANIC CHEMISTRY-SOME BASIC PRINCIPLES AND TECHNIQUES | HYDROCARBONS | ENVIRONMENTAL CHEMISTRY

GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 17 are also short answer questions and carry 3 marks each.
- (v) Q. no. 18 is a value based question and carries 4 marks.
- (vi) Q. no. 19 and 20 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.
- Write the names of the products obtained when C—Cl bond of ethyl chloride undergoes heterolytic fission.
- 2. Why do the C—C bonds rather than the C—H bonds break during pyrolysis of alkanes?
- 3. What are primary and secondary pollutants?
- 4. For testing halogens in an organic compound with AgNO₃ solution (Lassaigne's test), sodium extract is acidified with dilute HNO₃. What will happen if the extract is acidified with dilute H₂SO₄ in place of dilute HNO₃?
- 5. Acetylene is acidic but it does not react with NaOH or KOH. Give reason.
- 6. An alkane has the molecular mass equal to 72 g/mol. Give the possible structural isomers along with their IUPAC names.

OR

A reaction is carried out using aniline as a reactant as well as a solvent. How will you remove unreacted aniline?

7. Compound (A), C_6H_{12} decolourises bromine dissolved in carbon tetrachloride. Reaction of

(*A*) with alkaline KMnO₄ yields only (*B*) which is potassium salt of an acid. Write the structures and IUPAC names of the compounds (*A*) and (*B*).

- 8. What do you understand by Greenhouse effect? What are the major Greenhouse gases?
- 9. Which of the two, O₂NCH₂CH₂O⁻ or CH₃CH₂O⁻ is expected to be more stable and why?
- **10.** Explain why the following systems are not aromatic?

- **11. (i)** What is smog? How is classical smog different from photochemical smog?
 - (ii) What are biodegradable and non-biodegradable pollutants?
- 12. (i) Explain how the following mixtures can be separated :
 - (a) Benzoic acid and naphthalene
 - (b) *o*-Nitrophenol and *p*-nitrophenol



- (ii) The R_f values of A and B in a mixture determined by TLC in a solvent mixture are 0.65 and 0.42 respectively. If the mixture is separated by column chromatography using the same solvent mixture as a mobile phase, which of the two components, A or B, will elute first? Explain.
- **13.** How will you prepare *cis*-pent-2-ene and *trans*-pent-2-ene by starting with ethyne?
- **14. (i)** What do you mean by ozone hole? What are its consequences?
 - (ii) From where does ozone come in the photochemical smog?
- 15. Give reasons for the following :
 - (i) SO_3 acts as an electrophile.
 - (ii) Lassaigne's test is not successful for diazonium salts.
 - (iii) Alkyl groups act as electron donors when attached to a π -system.
- **16. (i)** Explain the following :
 - (a) *tert*-Butylbenzene does not give benzoic acid on oxidation with acidic $KMnO_4$.
 - (b) $CH_2 = CH^-$ is more basic than $HC \equiv C^-$.
 - (ii) Predict the major product in the following reaction :

$$C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$$

OR

- (i) How will you convert benzene into(a) *p*-nitrobromobenzene
 - (b) *m*-nitrochlorobenzene?
- (ii) Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitution reactions with difficulty?
- **17. (i)** Explain the terms inductive effect and electromeric effect.
 - (ii) Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a)
$$Cl_3CCOOH > Cl_2CHCOOH$$

(b)
$$CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$$

18. Ms. Disha Agnihotri, a senior science teacher delivered a lecture on 'benign by design' topic to class 12 students during the science week. She explained in detail how green chemistry reduces pollution through fundamental breakthroughs

in designing and redesigning chemical processes with an eye towards making them environment friendly.

- (i) What values are displayed by the teacher?
- (ii) What is Green chemistry?
- (iii) Explain how green chemistry can be applied to
 - (a) reduce the use of synthetic detergents
 - (b) reduce the use of halogenated solvents in dry cleaning and that of chlorine in bleaching?
- **19.** (i) Explain the following :
 - (a) Sodium extract is made acidic with acetic acid before the addition of lead acetate in the test of sulphur.
 - (b) In the test of nitrogen, freshly prepared solution of ferrous sulphate is always used.
 - (c) During the test for halogens, sodium extract is first boiled with a few drops of conc. HNO₃.
 - (ii) In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

OR

(i) Classify the following reactions in one of the reaction types.

(a)
$$CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$$

(b) $(CH_2)CH_2CH_2 + HCI_2$

(b)
$$(CH_3)_2 C = CH_2 + HCI \rightarrow$$

 $(CH_3)_2 C(Cl) - CH_3$

(c)
$$CH_3CH_2Br + HO^- \longrightarrow CH_2 = CH_2 + H_2O + Br^-$$

(d)
$$(CH_3)_3C - CH_2OH + HBr \longrightarrow$$

 $(CH_3)_2CBrCH_2CH_3 + H_2O$

- (ii) Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.
 - (a) C_6H_5OH (b) $C_6H_5NO_2$
 - (c) $CH_3CH=CHCHO$
- 20. (i) An alkene 'A' contains three C—C σ-bonds, eight C—H σ-bonds, and one C—C π-bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write the IUPAC name of 'A'.
 - (ii) Predict the major products of the following reactions and explain their formation.

(a)
$$H_3C-CH=CH_2 \xrightarrow{(PhCOO)_2}{HBr}$$

18

(b)
$$H_3C-CH=CH_2 \xrightarrow{HBr}$$

(iii) Which of the following has larger dipole moment? Explain.1-Butyne or 1-Butene

OR

- (i) Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+ .
 - (a) Chlorobenzene; 2,4-dinitrochlorobenzene; *p*-nitrochlorobenzene
 - (b) Toluene, *p*-nitrotoluene, *p*-dinitrobenzene
- (ii) What will be the product obtained as a result of the following reaction and why?

+ H₃C-CH₂-CH₂Cl
$$\xrightarrow{\text{anhy. AlCl}_3}$$

(iii) How will you convert hexane into benzene?

SOLUTIONS

1.
$$\begin{array}{c} CH_{3}CH_{2}-Cl \xrightarrow{\text{Heterolytic cleavage}} CH_{3}CH_{2}+\bar{C}l \\ Ethyl chloride & Ethyl \\ carbocation & ion \end{array}$$

- 2. Bond energy of C—C bonds (83.0 kcal/mol) is lower than the bond energy of C—H bond (98.8 kcal/mol) thus, C—C bonds break more easily than C—H bonds.
- 3. Primary pollutants are those which enter directly into the atmosphere due to natural or human activity, *e.g.*, NO while secondary pollutants are those which are formed as a result of reaction between primary pollutants, *e.g.*, PAN (Peroxyacetylnitrates).
- **4.** Silver sulphate (Ag_2SO_4) will be precipitated in place of silver halide and white precipitate will be formed even in the absence of halogen.
- 5. Acetylene is a very weak acid thus, it does not react with NaOH or KOH but reacts with a very strong base such as NaNH₂.

6. Molecular mass of alkane = 72 g/mol.

$$\Rightarrow C_n H_{2n+2} = 72 g/mol$$
or $12n + 2n + 2 = 72$ or $n = 5$,
So, the alkane is $C_5 H_{12}$.
Structural isomers are :
(i) $CH_3CH_2CH_2CH_2CH_3$ (Pentane)
(ii) $CH_3-CH-CH_2CH_3$ (2-Methylbutane)
 CH_3
(iii) CH_3-C-CH_3 (2,2-Dimethylpropane)
 CH_3
(iii) CH_3-C-CH_3 (2,2-Dimethylpropane)
 CH_3

OR

The boiling point of aniline is very high (457 K). If aniline (large excess) is distilled from a small amount of the product by simple distillation, it may cause decomposition of the product. Therefore, to avoid decomposition of the product, aniline is removed either by vacuum distillation or by steam distillation.

 The molecular formula C₆H₁₂ suggests that the compound (*A*) may be an alkene or a cycloalkane. As (*A*) decolourises Br₂ dissolved in CCl₄, it must be an alkene.

Oxidation of (A) with alkaline KMnO₄ yields only one salt of an acid, the alkene (A) must be symmetrical, *i.e.*, hex-3-ene.

Reactions are as follows :

ar

$$CH_{3}CH_{2}CH = CHCH_{2}CH_{3} \xrightarrow{Br_{2} \text{ in}} CCl_{4} \rightarrow CH_{3}CH_{2}CHBrCHBrCH_{2}CH_{3}$$

$$3, 4-Dibromohexane$$
and
$$CH_{3}CH_{2}CH = CHCH_{2}CH_{3} \xrightarrow{Alk. KMnO_{4}} 2CH_{3}CH_{2}COOK$$
Potassium propanoate

n propa (B)

8. The warming of the earth or global warming due to re-emission of sun's energy absorbed by the earth followed by its absorption by CO_2 molecules and H_2O vapour present near the earth's surface and then its radiation back to the earth is called greenhouse effect.

Though CO_2 is the main gas responsible for greenhouse effect, there are some other greenhouse gases also, *e.g.*, methane, chlorofluorocarbons, ozone, nitrous oxide and water vapours.

$$O_2 N - CH_2 - CH_2 - O^- \qquad CH_3 - CH_2 - O^-$$

Any ion, whether positively charged or negatively charged, is stable if it is somehow able to diminish the charge appearing on it or, is able to delocalise (spread) the charge on more than one atom. This dispersal/delocalisation of negative charge happens in (I) due to the presence of $-NO_2$ group which is electron withdrawing in nature. Due to this electron withdrawal, the charge on the oxygen atom is dispersed and the ion (I) becomes more stable as compared to ion (II).

$$O_{\mathbb{N}}$$
 N-««CH₂-«CH₂ «O⁻

CHEMISTRY TODAY | DECEMBER '15

19

10. (i) Due to the presence of sp^3 hybridised carbon, the system is not planar hence, it is not aromatic.

- (ii) Cyclooctatetraene is tub-shaped *i.e.*, not planar and has 8π electrons. Therefore, the system is not aromatic.
- 11 (i) The presence of smoke in fog is called smog. Classical smog occurs in cool and humid climate when smoke and SO₂ are suspended in air and it is reducing in nature.

On the other hand, photochemical smog occurs in warm, dry and sunny climate. It is produced by the action of light on unsaturated hydrocarbons and NO_r in air and, it is oxidising in nature.

- (ii) Biodegradable pollutants are decomposed by bacteria while non-biodegradable pollutants cannot be decomposed or they degrade slowly.
- 12. (i) (a) Both these solids undergo sublimation on heating. So, the mixture is heated with water, when only benzoic acid dissolves. Upon filtration naphthalene is separated. The solution on cooling gives the crystals of benzoic acid.

Alternatively, the mixture is treated with strong aqueous NaOH (or NaHCO₃) solution. The benzoic acid is converted into sodium benzoate while naphthalene is unaffected. The naphthalene is separated by filteration. The filtrate is treated with dil. HCl to regenerate benzoic acid.

 $C_6H_5COOH + NaOH_{(aq.)} \longrightarrow C_6H_5COONa$ $+ H_2O$

$$C_6H_5COONa + HCl_{(dil.)} \longrightarrow C_6H_5COOH + NaCl_{(aq.)}$$

- (b) o-Nitrophenol and p-nitrophenol can be separated by steam distillation. o-nitrophenol being volatile distils over along with water while *p*-nitrophenol being non-volatile remains in the flask.
- (ii) Since the R_f value of 'A' is 0.65, therefore it is less strongly adsorbed as compared to component 'B' with R_f value of 0.42. Therefore, on extraction of the column, 'A' will elute first.

13. HC = CH
$$\xrightarrow{\text{Na, NH}_{3(l)}}$$
 HC = C⁻Na⁺ $\xrightarrow{\text{CH}_{3}\text{I}}$
Ethyne
CH₃-C = C⁻Na⁺ $\xleftarrow{\text{Na, NH}_{3(l)}}$ CH₃-C = CH
Sodium propynide
CH₃CH₂I
-NaI
CH₃-C = C-CH₂CH₃
Pent-2-yne
H₂/Pd-BaSO₄ + S
or quinoline
(Lindlar's
catalyst)
CH₃-C = C
CH₂CH₃
CH₃-C = C
CH₂CH₃
CH₃-C = C
CH₂CH₃
CH₃-C = C
CH₂CH₃
CH₃-C = C
H
CH₃-C = C
CH₂CH₃
CH₃-C = C
CH₂CH₃

- The depletion of ozone layer is termed as 14. (i) ozone hole. It was first reported by a group of scientists working in Antarctica in 1980s. Ozone layer is responsible for prevention of infiltration of UV rays which has the potential to cause serious damage to plants, animals and human life. Due to depletion of this O₃ layer, these harmful rays will find an easy route into the earth's atmosphere and create problems such as mutation of cells leading to cancer of the skin or increased transpiration in plants and reduced water level in soil. Increase in UV radiations damages paints and fibres causing them to fade faster.
 - **(ii)** In presence of sunlight, NO₂ present in the air undergoes photolysis to form NO and atomic oxygen. The atomic oxygen then combines with the molecular oxygen to form ozone.

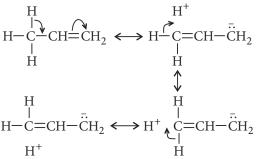
$$NO_2 \xrightarrow{n\nu} NO + O, \quad O + O_2 \longrightarrow O_3$$

15. (i) Due to resonance, sulphur acquires positive charge and therefore, SO₃ acts as an electrophile.

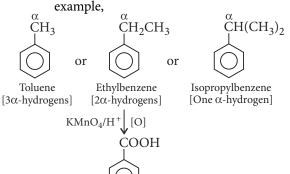
$$\bigcup_{i=1}^{O} \longleftrightarrow_{i=1}^{O} \longleftrightarrow_{i=1}^{O}$$

- (ii) Diazonium salts, $C_6H_5N_2^+X^-$, are unstable and reactive compounds. Therefore, when heated in a fusion tube with sodium to prepare Lassaigne's extract, they immediately get decomposed to give N₂ gas and therefore, NaCN is not formed.
- (iii) Due to hyperconjugation, alkyl groups act as electron donors when attached to a π -system as shown :

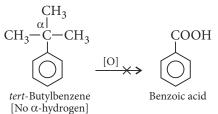




16. (i) (a) Alkylbenzenes in which the alkyl groups contain one or more α -hydrogens or benzylic hydrogen on vigorous oxidation with acidic KMnO₄ ultimately give the corresponding benzoic acids irrespective of the length of the carbon chain. For



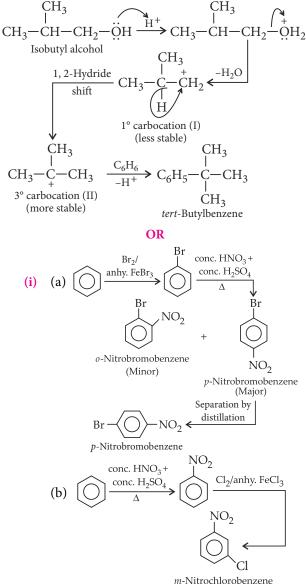
Benzoic acid tert-Butylbenzene, on the other hand, does not contain any α -hydrogen or benzylic hydrogen and hence does not undergo oxidation easily to give benzoic acid.



(b) $CH_2 = CH^{-1}$ is the conjugate base of the acid $H_2C = CH_2$ and $HC \equiv C^-$ is the conjugate base of the acid HC≡CH. We know that stronger the acid, weaker is the conjugate base. Since, HC≡CH is stronger acid than $CH_2 = CH_2$, therefore, $CH_2 = CH^-$ is a stronger base than $HC \equiv C^{-}$.

(ii) In presence of conc. H_2SO_4 , isobutyl alcohol first gives 1° carbocation (I) which then rearranges to the more stable 3° carbocation (II)

by 1, 2-hydride shift. Carbocation (II) then reacts with benzene to form tert-butylbenzene.



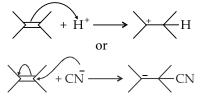
- (ii) Due to the presence of electron cloud containing 6 π -electrons above and below the plane of the ring, benzene is a rich source of electrons. Consequently, it attracts the electrophiles towards it and repels nucleophiles. As a result, benzene undergoes electrophilic substitution reactions easily and nucleophilic substitution reactions with difficulty.
- 17. (i) Inductive effect : Polarisation of σ -bond due to the electron donating or electron withdrawing nature of groups attached is called inductive effect.

e.g., Attachment of Cl, an electronegative atom

to an ethane molecule causes the carbons to carry a δ^+ charge.

 $\begin{array}{c} \operatorname{carry a} \delta^+ \operatorname{charge.}_{\delta^+} \\ \operatorname{Cl} \stackrel{\delta^-}{\dashrightarrow} \operatorname{CH}_2 \stackrel{\delta^+}{\dashrightarrow} \operatorname{CH}_3 \end{array}$

Electromeric effect : In the presence of an attacking reagent, the π -electron cloud in a multiple bonded compound tends to get polarised. Such an effect is termed as temporary effect and the original condition is restored if the reagent is removed.



(ii) (a) The given order of acidity can be explained by -*I* effect. Cl is an electronegative atom which withdraws electrons from the adjacent carbon atom. This in turn pulls electrons from the carboxylic group which results in increased acidity. Thus, more the number of Cl atoms, higher is the acidic strength.

 $Cl_3CCOOH > Cl_2CHCOOH$

> ClCH₂COOH

(b) This is an example of +I effect. $-CH_3$ group is an electron donating group and increases the electron density of the adjacent carbon and this transfers the electron density on the -COOH group. As a result, the release of H as H⁺ becomes difficult and the acidity decreases.

So, if the number of such $-CH_3$ groups is more on the α -carbon, then the acidic strength decreases.

- **18. (i)** The teacher showed her concern towards the environment and tried to spread awareness regarding green chemistry.
 - (ii) Green chemistry can be defined as the design, development and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and environment.
 - (iii) (a) Soaps should be used in place of detergents because soaps are 100% biodegradable and do not cause any pollution problem. Nowadays, soft detergents are available which are biodegradable. They can be used in place of 'hard detergents' which are non-biodegradable.
 - (b) In dry cleaning, liquefied CO₂ along with

a suitable detergent should be used and for bleaching, hydrogen peroxide should be used which gives better results and is not harmful.

- 19. (i) (a) Lead acetate is hydrolysed by NaOH present in sodium extract. It is neutralised first with acetic acid before the addition of lead acetate.
 - (b) Ferrous sulphate gets hydrolysed if its solution is stored.
 - (c) During the test for halogens, sodium extract is first boiled with a few drops of conc. HNO_3 to decompose NaCN or Na₂S if present in the sodium extract.
 - (ii) Mass of organic sulphur compound = 0.468 g
 - Mass of $BaSO_4 = 0.668 \text{ g}$ 1 mol of $BaSO_4 = 233 \text{ g}$ 233 g of $BaSO_4$ contains 32 g of S.
 - \therefore 0.668 g of BaSO₄ contains

$$\frac{0.668 \times 32}{233} = 0.09174 \,\mathrm{g}$$

0.09174 g S is present in 0.468 g of the compound.

 $\Rightarrow \% \text{ of S in compound} = \frac{0.09174}{0.468} \times 100$ = 19.6%

OR

(i) (a) $CH_3CH_2Br + SH^- \rightarrow CH_3CH_2SH + Br^-$

Here HS⁻, a nucleophile displaces Br⁻ from the bromoalkane. Since, the reaction is brought about by a nucleophile and substitution occurs thereafter, the reaction will be termed as a nucleophilic substitution reaction.

(b) $\underset{H_3C}{H_3C} C = CH_2 + HCl \rightarrow \underset{H_3C}{\overset{Cl}{\longrightarrow}} C = CH_3$

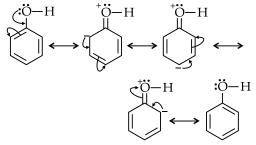
Here, alkene due to its high electron density undergoes electrophilic attack. Thus, H^+ and Cl^- ions are added to the alkene. Hence, the reaction is an electrophilic addition reaction.

(c) $CH_3CH_2Br + OH^- \rightarrow CH_2 = CH_2 + H_2O + Br^-$

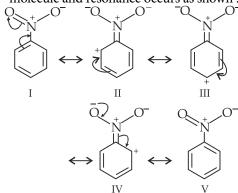
Here, there is no atom which is displaced or substituted. Although the reaction is brought about by a nucleophile OH⁻, it is not a nucleophilic substitution. It is an elimination reaction as HBr molecule has been removed from the reactant.



- (d) $(CH_3)_3C CH_2 OH + HBr \longrightarrow$ $(CH_3)_2CBrCH_2CH_3 + H_2O$ This is an example of a rearrangement followed by nucleophilic substitution. Initially, a 1° carbocation is formed which rearranges to produce a more stable 3° carbocation. Finally, Br⁻ attacks the carbocation and product is formed.
- (ii) (a) Resonance structures of phenol are :



(b) $-NO_2$ is an electron withdrawing group. As a result, it polarises the benzene molecule and resonance occurs as shown :



(c) $CH_3CH = CHCHO$ is an α , β -unsaturated aldehyde where the C=C gets polarised due to the neighbouring electron withdrawing -CHO group.

$$H_{3}C-HC=CH-C \xrightarrow{(O)}_{H} H_{3}C-HC=CH \xrightarrow{C}C^{O^{-}}_{H} H_{3}C-HC \xrightarrow{C}CH \xrightarrow{C$$

20. (i) An aldehyde with molar mass of 44 u is ethanal, $CH_3CH=O$. Thus, the alkene 'A' which on ozonolysis gives two moles of ethanal can be formed by removing oxygen atoms from two moles of ethanal and joining them by a double bond as shown below :

$$\begin{array}{c} CH_{3}CH=O \quad O = CHCH_{3} \Leftrightarrow CH_{3} - CH = CH - CH_{3} \\ Ethanal \quad Ethanal \quad But-2-ene \end{array}$$

required, but-2-ene has three As C–C σ -bonds, eight C–H σ -bonds and one C—C π -bond.

(ii) (a) In presence of peroxide, addition of HBr to propene follows anti-Markovnikov's rule and hence, gives 1-bromopropane as the major product. The reaction occurs through a free radical mechanism via a more stable free radical intermediate as shown in the reaction :

$$CH_{3}-CH=CH_{2}+\dot{B}r \xrightarrow{Slow} CH_{3}-\dot{C}H-CH_{2}Br \xrightarrow{H-Br}_{Fast}$$

$$2^{\circ} free radical$$

$$CH_{3}-CH_{2}-CH_{2}Br + \dot{B}r \xleftarrow{I-Br}_{1-Bromopropane}$$

(b) In absence of peroxides, addition of HBr to propene follows Markovnikov's rule and hence, gives 2-bromopropane as the major product. The reaction occurs through ionic mechanism via a more stable carbocation intermediate as shown below :

$$CH_{3}-CH=CH_{2}+H^{+}\xrightarrow{Slow}CH_{3}-CH-CH_{3}\xrightarrow{Br^{-}}_{Fast}$$

$$2^{\circ} \text{ free radical}$$

$$CH_{3}-CH-CH_{3}\xleftarrow{Br}$$

2-Bromopropane

(iii) The direction of dipole moments of individual bonds in 1-butyne and 1-butene are shown below :

$$CH_{3}CH_{2} \stackrel{sp^{3}}{\rightleftharpoons} C \stackrel{sp}{\equiv} C \stackrel{sp}{\equiv} C \stackrel{sp}{\equiv} C \stackrel{sp}{\equiv} C \stackrel{sp}{\equiv} C \stackrel{sp}{\equiv} C \stackrel{sp^{3}}{\leftarrow} H$$

$$CH_{3}CH_{2} \stackrel{sp^{2}}{\leftarrow} \stackrel{sp^{2}}{\leftarrow} \stackrel{sp^{2}}{\leftarrow} H$$

$$H \stackrel{sp_{3}}{\leftarrow} C \stackrel{sp^{2}}{\leftarrow} \stackrel{sp}{\leftarrow} H$$

$$H \stackrel{sp_{3}}{\leftarrow} H$$

The resultant dipole moment of both 1-butyne and 1-butene is due to the dipole moments of CH₃CH₂-C and C-H bonds which oppose each other. Since a sp carbon is more electronegative than a sp^2 carbon, therefore, the dipole moment of $CH_3CH_2 - C$ bond in 1-butyne is more than that of CH_3CH_2-C bond in 1-butene. As a result, the dipole moment of 1-butyne is more than that of 1-butene.

OR

Contd. on page no.77



EXAMINER'S MIND CLASS

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

p-BLOCK ELEMENTS | ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

(a) 2, 2

(c) 3, 2

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- **1.** CO_2 is isostructural with
 - (a) HgCl₂ (b) SnCl₂
 - (c) C_2H_4 (d) NO_2

2. The IUPAC name of $H_2N - C - CH_2 - COOH$ is

- (a) 3-amino-3-oxopropanoic acid
- (b) 3-amidopropanoic acid
- (c) 2-amidoethanoic acid
- (d) 2-carbamoylethanoic acid.
- 3. Which of the following substances does not act as a Lewis acid?

(a)	AlCl ₃	(b)	$SnCl_4$
(4)	11013	(0)	011014

(c)	FeCl ₃	(d)	AlCl ₃ ·6H ₂ O

4. In which of the following two carbon atoms are differently hybridised?

$$CH_2 = \dot{C}H \qquad CH_3 \bar{C}HCH_3 \qquad CH_2 = \bar{C}H \qquad II \qquad III \qquad IIII \qquad III \qquad III \qquad$$

- 5. When Sn is treated with conc. HNO₃
 (a) it is converted into stannous nitrate
 - (b) it is converted into stannic nitrate
 - (c) it is converted into metastannic acid
 - (d) it becomes passive.
- 6. Prussian blue can be represented as $\operatorname{Fe}[\operatorname{Fe}(\operatorname{CN})_6]^-$

Oxidation numbers of Fe atoms indicated by x and y are respectively

CHEMISTRY TODAY | DECEMBER '15

7.	When PbO_2 is reacted with HCl then the gas coming
	out is

(b) 2, 3

(d) 3, 3

- (a) O_2 (b) Cl_2 (c) H_2 (d) $CO + H_2$
- 8. Which of the following statements is false?
 - (a) Feeble acids and bases are weaker than H_2O .
 - (b) Weak acids are weaker than H_3O^+ but stronger than H_2O .
 - (c) Weak bases are weaker than OH^- but stronger than H_2O .
 - (d) None of these.
- 9. Select the incorrect statement.
 - (a) B_2H_6 has all B—H bonds equal.
 - (b) AlH₃ is colourless solid and is polymeric containing Al—H—Al bridges.
 - (c) LiAlH₄ is an ionic compound.
 - (d) Aluminium halides (Al X_3 where X =Cl, Br, I) have low melting points, are covalent and have the halogen-bridged dimeric structures.
- 10. Which of the following statements is correct?
 - (a) Singlet dimethylcarbene [(CH₃)₂C:] is more stable than the triplet [(CH₃)₂C].
 - (b) Singlet difluorocarbene $[F_2C:]$ is less stable than the corresponding triplet.
 - (c) Singlet carbene resembles free diradical while triplet carbene resembles a carbocation.
 - (d) None of these.
- 11. Dry powder fire extinguisher contains
 - (a) sand
 - (b) sand and Na₂CO₃
 - (c) sand and baking soda
 - (d) sand and K₂CO₃.



- 12. Arrange the following in decreasing order of solubility in water.
 - (a) I > III > II
 - (b) III > II > I
 - (c) II > III > I
 - (d) All are equally soluble
- 13. Mixture of $Al(OH)_3$ and $Fe(OH)_3$ can be separated by:
 - (a) HCl (b) NH₄OH
 - (c) NaOH (d) HNO₃
- 14. Which of the following is not stabilised by hyperconjugation?

(a)
$$CH_3 - CH_2$$
 (b) $\longrightarrow CH_2$
(c) $\stackrel{+}{\checkmark}$ (d) $\stackrel{-}{\checkmark}$

15. Which of the following is true?

- (a) Coke is found in nature.
- (b) Producer gas is a mixture of CO and H_2 .
- (c) CO is used in the extraction of Ni by Mond's process.
- (d) CO_2 can be prepared by dehydration of formic acid.
- 16. Solubility of an organic compound in water is 10 g/100 mL at 20°C and 60 g/100 mL at 70°C. 30 g of an impure organic compound is dissolved in 50 mL of water at 70°C and cooled to 20°C. Crystals formed weigh (1) 00

(a) 5 g	(b) 20 g
(c) 25 g	(d) 30 g

- 17. Which of the following statements is incorrect?
 - (a) The *meta*-position in nitrobenzene undergoes electrophilic substitution reaction because it is less deactivated when compared to ortho and para positions in nitrobenzene.
 - (b) The *meta*-position in phenol is more electron rich than the *meta*-position in nitrobenzene.

NHCOCH₃

(c) The benzene ring in is slightly NH_2

deactivated than the benzene ring in

- (d) $\overset{+}{C}F_3$ is less stable than $CF_3\overset{+}{C}H_2$.
- 18. The correct order of increasing stability of the following carbanions is

$$CH_2 = CH\bar{C}H_2 \quad CH_2 = \bar{C}H \quad (CH_3)_3\bar{C}$$

$$I \quad II \quad III$$

$$Ph_3\bar{C} \quad \bar{C}H_3$$

$$IV \quad V$$

(a) III < V < II < IV < I(b) II < III < V < IV < I

- (c) II < III < V < I < IV
- (d) III < V < II < I < IV

Ш

Π

- **19.** Borazine $B_3N_3H_6(A)$ is converted into disubstituted product $B_3N_3H_4X_2(B)$. Number of isomers of 'B' would be
 - (a) 2 (b) 4
 - (c) 6 (d) none of these.
- 20. Organic compound of the molecular formula $C_2H_2Br_2$ can exist in how many isomeric forms?
 - (a) 1 (b) 2
 - (c) 3 (d) 4

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

- 21. Which of the following equilibria represent(s) the actual source of proton in boric acid?
 - (a) $B(OH)_{3(aq)} + 2H_2O_{(l)} = H_3O_{(aq)}^+ + [B(OH)_4]_{(aq)}^-$
 - (b) $3B(OH)_{3(aq)} \rightleftharpoons [B_3O_3(OH)_4]_{(aq)}^- + 2H_2O_{(l)}$ (In neutral or basic solution)
 - (c) $B(OH)_3 \Longrightarrow H_2BO_3^+ + H^+$
 - (d) All of the above
- 22. Which of the following statement(s) is/are correct?
 - (a) HCN and HNC are functional isomers.
 - (b) HCN and HNC are tautomers.
 - (c) *R*—CN and *R*—NC are functional isomers.
 - (d) $R_3 N^+$ shows -I effect.
- 23. Which of the following is/are sub-oxides?
 - (b) N₂O (a) C_3O_2
 - (c) PbO_2 (d) CO₂
- 24. Which of the following have zero dipole moment? (a) *p*-Dichlorobenzene (b) Benzene-1, 4-diol
 - (c) Fumaric acid (d) Maleic acid
- **25.** The difference in properties of CH_4 and SiH_4 is due to
 - (a) large difference in the electronegativity of carbon and silicon
 - (b) large difference in size of carbon and silicon atoms
 - (c) the inability of carbon to expand its octet
 - (d) the inability of silicon to form double bonds.



SECTION - III

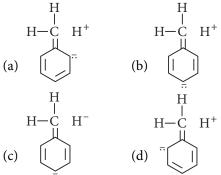
Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Hyperconjugation is a general stabilising interaction. It involves delocalisation of *s*-electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p*-orbital. The *s*-electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared *p*-orbital. Hyperconjugation is a permanent effect.

26. Which of the following is incorrect hyperconjugative structure?

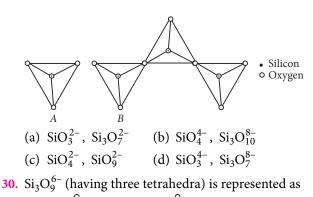


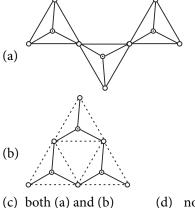
- 27. Which of the following has highest heat of hydrogenation?
 - (a) Ethylene (b) But-1-ene
 - (c) Isobutylene (d) Tetramethylethylene
- **28.** Which of the following has highest heat of combustion?
 - (a) Isobutylene (b) But-1-ene
 - (c) Tetramethylethylene (d) But-2-ene

Paragraph for Questions 29 to 31

The basic structural unit of silicates is SiO_4^{4-} in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion. In silicates, either the discrete unit is present or a number of such units are joined together *via* corners by sharing 1, 2, 3 or 4 oxygen atoms per silicate unit. When silicate units are linked together, they form chain, ring, sheet or three-dimensional structures.

29. Structures '*A*' and '*B*' represent different silicate anions. Their formulae are respectively





(d) none of these.

- **31.** The silicate anion in the mineral kinoite is a chain of three SiO_4^{4-} tetrahedra that share corners with adjacent tetrahedra. The mineral also contains Ca^{2+} ions, Cu^{2+} ions, and water molecules in a 1 : 1 : 1 ratio. The mineral is represented as
 - (a) CaCuSi₃O₁₀·H₂O
 - (b) CaCuSi₃O₁₀·2H₂O
 - (c) $Ca_2Cu_2Si_3O_{10} \cdot 2H_2O$
 - (d) none of these.

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the compounds given in List I with their uses given in List II and select the correct answer using the code given below the lists :

	List I		List II
P.	Boric acid	1.	Friedel-Crafts
			acylation
Q.	Borax	2.	Mild antiseptic
R.	Aluminium chloride	3.	Washing powder
S.	Sodium peroxoborate	4.	Buffer



	Р	Q	R	S
(a)	1	2	3	4
(b)	2	3	4	1
(c)	2	4	1	3
(d)	4	3	2	1

List I

33. Match the phenomena given in List I with their descriptions given in List II and select the correct answer using the code given below the lists :

List II

- Q. Resonance 2. Strong effect
- R. No bond 3. Permanent effect resonance
- S. Electromeric 4. Delocalisation of π -electrons effect
- P
 Q
 R
 S

 (a)
 1
 4
 3
 2

 (b)
 4
 3
 1
 2

 (c)
 3
 4
 1
 2
- (1)
- (d) 1 4 3 2
- **34.** Match the List I with List II and select the correct answer using the code given below the lists :

	Lis	st I				List II
Р.	C_8	Κ			1.	Producer gas
Q.	SiC	SiC			2.	Paramagnetic
R.	CC) + N	\mathbf{V}_2		3.	Carborundum
S.	CC), H ₂	, CC	0 ₂ , CH ₄	4.	Coal gas
	Р	Q	R	S		
(a)	2	3	1	4		
(b)	1	2	3	4		
(c)	4	3	2	1		
(d)	2	1	4	3		

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 35. Assertion : Tl³⁺ acts as an oxidising agent.
 Reason : Due to inert pair effect, Tl⁺ is more stable than Tl³⁺.
- **36. Assertion :** In case of volatile compounds, vapour density is one-half of the molecular weight.

Reason : Vapour density is the other name of density.

- **37.** Assertion : Hybridisation of boron in B_2H_6 is sp^3 and geometry of boron is tetrahedral. **Reason :** Three centre-two electron bonds are present in B_2H_6 molecule.
- **38.** Assertion : Lithium is not used in Lassaigne's test. Reason : Lithium generally forms covalent compounds.
- **39. Assertion :** Many metals produce coloured beads with borax.

Reason : Borax forms a glassy bead on heating which optically influences light in a way that is characteristic of the metal involved.

40. Assertion : Heterolytic fission of $CH_3CH_2CH_3$ gives CH_3CH_2 and CH_3^- .

Reason : CH_3CH_2 is more stable than CH_3 , but CH_3CH_2 is less stable than CH_3 .

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

- **41.** Number of resonating structures possible in isopropyl carbocation is
- **42.** Number of electrons transferred to vacant 2*p*-orbital of boron by fluorine in BF₃ is
- **43.** Deep violet coloured complex formed when sodium extract of the organic compound containing sulphur is treated with sodium nitroprusside has the formula $Na_2[Fe(CN)_xNOS]$. The value of *x* is
- **44.** When diborane reacts with excess of ammonia at low temperature, then it gives B_2H_6 ·2NH₃ which is comprised of *x* number of ions. The value of *x* is
- **45.** Number of π -electrons in the following structure is



- **46.** Percentage of CO_2 in carbogen mixture used in treatment of central retinal artery occlusion is
- **47.** Number of groups amongst the following that show *–I* effect is

$$-CH_3$$
, CH_3 , CH_- , $-NO_2$, $-CHO$, $-COOH$, CH_3CH_2 -

CHEMISTRY TODAY | DECEMBER '15

27

- **48.** When stannous oxalate is heated then the number of gaseous products formed is
- **49.** In a compound C, H and N are present in 9:1:3.5 by weight. If molecular weight of the compound is 108, the number of N atoms present in the molecular formula will be
- **50.** In the compound beryl, number of oxygen atoms shared by one silicate tetrahedron is

SOLUTIONS

1. (a) : CO_2 is isostructural with HgCl₂ because both have linear structure.

2. (d):
$$(H_2NOC + CH_2 - COOH_2)$$

2-Carbamoylethanoic acid

3. (d): AlCl₃⋅6H₂O does not act as a Lewis acid because it exists as [Al(H₂O)₆]Cl₃, *i.e.*, Al³⁺ forms coordinate bonds with 6H₂O molecules.

AlCl₃ is electron deficient because octet of Al is not complete therefore, it acts as a Lewis acid.

 $SnCl_4$ is electron deficient because it has vacant *d*-orbitals and can accept negatively charged ion. Hence, it is a Lewis acid.

FeCl₃ is electron deficient because its octet is not complete therefore, it is a Lewis acid.

4. (d):
$$CH_2 = \overset{-}{C}H$$
 $CH_3 \overset{-}{Sp^3} \overset{-}{sp^3} \overset{-}{sp^3} \overset{-}{sp^2} \overset{-}{sp^2} \overset{-}{sp^2}$
I II III
 $CH \equiv \overset{-}{C} \overset{-}{sp} \overset{-}{sp^2} \overset{-}{sp^3} \overset{-}{sp^3$

5. (c) :
$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

Metastannic acid

- 6. (c) : Prussian blue, $\operatorname{Fe}[\operatorname{Fe}(\operatorname{CN})_6]^-$ is formed when Fe^{3+} salts react with $[\operatorname{Fe}^{\mathrm{II}}(\operatorname{CN})_6]^{4-}$ $\operatorname{Fe}^{3+} + [\operatorname{Fe}(\operatorname{CN})_6]^{4-} \longrightarrow \operatorname{Fe}^{\mathrm{III}}[\operatorname{Fe}^{\mathrm{II}}(\operatorname{CN})_6]^-$ Thus, x = 3 and y = 2.
- 7. (b): PbO_2 oxidises HCl to Cl_2 . $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$
- (d): Weak and feeble nature of an acid (or a base) is compared with H₂O which acts both as an acid as well as a base.
 In general, weak acid > H₂O > feeble acid

h general, weak acid > H_2O > feeble acid weak base > H_2O > feeble base

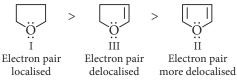
$$: \stackrel{:}{F} - C: \longleftrightarrow : \stackrel{:}{F} = C: \longleftrightarrow : \stackrel{:}{F} - C:$$

$$: \stackrel{!}{F} : : \stackrel{:}{F} : : \stackrel{:}{F} : \stackrel{:}{F} : \stackrel{:}{F} :$$
onance stabilisation of singlet diffuorocarb

Resonance stabilisation of singlet diffuorocarbene

Thus, $(CH_3)_2\dot{C} > (CH_3)_2C$: and $F_2\dot{C} < F_2C$: Triplet Singlet Triplet Singlet Also, singlet carbene resembles a carbocation and a triplet carbene resembles a free diradical.

- **11.** (c) : Mixture of sand (SiO_2) and baking soda $(NaHCO_3)$ is used as a dry powder fire extinguisher.
- 12. (a) : Higher the electron density on O, stronger is the H-bond with water and thus, more is the solubility. Thus, solubility of the three ethers follows the order :



13. (c) : NaOH dissolves $Al(OH)_3$ while $Fe(OH)_3$ remains insoluble.

$$NaOH + Al(OH)_3 \longrightarrow Na[Al(OH)_4]$$

Soluble

- 14. (b): Hyperconjugation is the delocalisation of sigma electrons with π -bond. In carbocation, hyperconjugation is possible only when α -hydrogen is present, so in carbocations (a), (c) and (d) hyperconjugation is possible while (b) is stabilised by the interaction of the cyclopropyl bonding orbitals with the vacant *p*-orbital of carbon.
- **15.** (c) : Coke is not found in nature. It is an artificial product. CO_2 cannot be formed by dehydration of formic acid.

HCOOH
$$\xrightarrow{\text{Conc. H}_2\text{SO}_4}$$
 CO + H₂O

Producer gas is a mixture of CO and N₂.

16. (c) : At 70°C, 100 mL water can dissolve organic compound = 60 g



: At 70°C, 50 mL water can dissolve organic compound = 30 g

At 20°C, 100 mL water can dissolve organic compound = 10 g

: At 20°C, 50 mL water can dissolve organic compound = 5 g

Hence, solute crystallised = (30 - 5) g = 25 g

 NO_2

OH

, the $-NO_2$ group deactivates the 17. (d): In benzene ring, *i.e.*, all the positions are deactivated but the deactivation at ortho and para-positions are more than that at the meta-position.

-OH group activates all the positions In in benzene ring but ortho and para are more activated than meta. Hence, meta-position in nitrobenzene is deactivated while meta-position in phenol is activated. So, meta-position in phenol is more electron rich than in nitrobenzene. $NH-C-CH_3$ due to the lone pair of In \cap

electrons in conjugation with -C- group, the

resonating structure is deactivated. Hence, ring is

benzene in -CH₃, the benzene ring is slightly NH 0

deactivated than the benzene ring in

In $\dot{C}F_3$, +ve charge is dispersed due to back bonding of lone pair of electrons from fluorine with vacant *p*-orbitals of C while in CF_3CH_2 due to -I effect of fluorine, the +ve charge is intensified and thereby, it is destabilised.

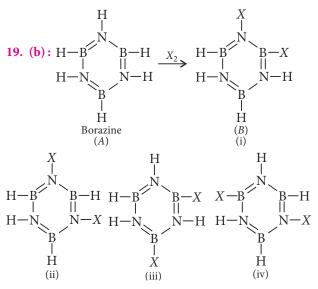
18. (d):
$$(CH_3)_3\bar{C} < \bar{C}H_3 < CH_2 = \bar{C}H <$$

III V II
Least stable due to +*I* effect Stable due to -ve charge
on electronegative carbon
 $CH_2 = CH - \bar{C}H_2 < Ph_3\bar{C}$
I IV
Stable due to delocalization Most stable due to exten

of -ve charge

to extensive delocalisation of -ve charge on benzene ring

<



Four different isomers of 'B' are possible.

20. (c) : $C_2H_2Br_2$ can have the following structures :

BrCH=CHBr
$$CH_2$$
=CBr₂
(cis- and trans-) II

Structures I and II are position isomers, further structure I (not II) can show geometrical isomerism.

21. (a)

22. (a, b, c, d): Cyanide and isocyanide are different functional groups hence, HCN, HNC and RCN, RNC are functional isomers.

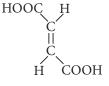
HCN is converted into HNC by 1, 2-hydrogen shift hence, they are tautomers.

In R_3 N, nitrogen has +ve charge hence, shows -I effect.

has zero dipole moment as both the

dipoles are equal and opposite.

(c): Fumaric acid is trans-isomer,



therefore, dipoles get cancelled.

CHEMISTRY TODAY | DECEMBER '15

29

(b) : Benzene-1, 4-diol, H has dipole moment

because both —OH groups are not in the same plane, their dipole moments do not get cancelled. (d) : Maleic acid is *cis*-isomer hence, it cannot have zero dipole moment.

25. (a, c)

- **26.** (c) : When *s*-electrons of C—H bond take part in hyperconjugation, H[−] cannot be formed rather H⁺ is formed.
- 27. (a) : Ethylene has highest heat of hydrogenation due to least hyperconjugation as there is no α -hydrogen atom. But-1-ene has two α -hydrogen atoms, isobutylene has six α -hydrogen atoms while tetramethylethylene has 12 α -hydrogen atoms.
- **28.** (b): Lesser the number of hyperconjugative structures, lesser will be the stability and thus, more will be the heat of combustion.

- **31.** (c) : The formula of silicate anion is $Si_3O_{10}^{8-}$. Thus, the mineral is represented as $Ca_2Cu_2Si_3O_{10} \cdot 2H_2O$.
- 32. (c)
- 33. (c) : P → 3; Inductive effect is a permanant effect.
 Q → 4; Resonance is the delocalisation of π-electrons.
 R → 1; No bond resonance or hyperconjugation is

delocalisation of sigma electrons with π -bond. S \rightarrow 2; Electromeric effect is very strong effect.

- **34.** (a): $P \rightarrow 2$; C_8K is paramagnetic because C_8^- contains one unpaired electron.
 - $Q \rightarrow 3$; SiC is carborundum.

 $R \rightarrow 1;$ A mixture of CO + N_2 is producer gas. S \rightarrow 4; A mixture of CO + H_2 + CO $_2$ + CH $_4$ is coal gas.

- 35. (a)
- **36.** (c) : Vapour density and density of a volatile organic compound are quite different.

Density = $\frac{\text{Mass}}{\text{Volume}}$

37. (a) : Due to 2e - 3c bond the hybridisation of B is sp^3 and the geometry is tetrahedral.

38. (a)

39. (c) : The metal cation on heating with borax bead produces corresponding coloured metaborate.

CHEMISTRY TODAY | DECEMBER '15

40. (a)

41. (7) : No. of resonating structures

= No. of hyperconjugative structures + 1.

42. (2): Fluorine transfers two electrons to vacant 2p-orbital of boron thus forming $p\pi$ - $p\pi$ bond.

43. (5):
$$S + 2Na \xrightarrow{\Delta} Na_2S$$

 $Na_2S + Na_2[Fe(NO)(CN)_5] \longrightarrow$
Sodium nitroprusside $Na_4[Fe(CN)_5NOS]$
Purple colour

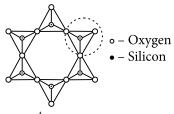
44. (2): The compound $B_2H_6 \cdot 2NH_3$ is ionic and comprises of $(H_3N \rightarrow BH_2 \leftarrow NH_3]^+$ and $[BH_4]^-$ ions.

(planar,
$$6\pi$$
-electrons, aromatic)

- **46.** (5) : Carbogen is a mixture of 95% O₂ and 5% CO₂.
- 47. (3): $-NO_2$, -CHO and -COOH groups show -I effect.
- 48. (2): (COO)₂Sn → SnO_(s) + CO_(g) + CO_{2(g)}
 Thus, CO and CO₂ are the two gaseous products formed.
- **49.** (2): Weight ratio: Molar ratio: $\begin{array}{rcl}
 C & H & N \\
 9 & 1 & 3.5 \\
 \frac{9}{12} & \frac{1}{1} & \frac{3.5}{14} \\
 = & \frac{3}{4} & \frac{1}{1} & \frac{1}{4}
 \end{array}$

Simplest ratio : 3 : 4 : 1 Empirical formula = C_3H_4N $(C_3H_4N)_n = 108$ $(12 \times 3 + 1 \times 4 + 14)n = 108$ $54 n = 108 \implies n = 108/54 = 2$ Molecular formula = $C_6H_8N_2$

50. (2) : Beryl is a cyclic silicate. The formula of Beryl is $Be_3Al_2(SiO_3)_6$. Every SiO_4^{4-} unit shares two O atoms. The structure



 SiO_4^{4-} is sharing two O atoms.

، ا



Maximize your chance of success, and high rank in JEE (Main and Advanced) / BITSAT by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

ACCELERATED F SERIES

PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS Unit SOME BASIC PRINCIPLES OF ORGANIC CHEMISTRY | HYDROCARBONS ORGANIC COMPOUNDS CONTAINING HALOGENS

PURIFICATION AND CHARACTERISATION **OF ORGANIC COMPOUNDS**

- Methods of Purification of Organic Compounds •
- **Qualitative Analysis**
- **Quantitative Analysis**
- Calculation of Empirical and Molecular Formula

TIPS TO REMEMBER

Purification

- The organic compounds extracted from natural sources or synthesised in the laboratory are
- The methods commonly used for purification are :

contaminated with small amounts of other similar compounds. In order to characterise them, it is essential to purify them.

Class XI-XII

- The methods employed for purification depend upon the nature of the substance (whether solid or liquid) and the type of impurities present in it.
- The purity of an organic compound is checked by determining one or more of its physical constants like melting point, boiling point etc.

Method	Used for separating	Examples
Crystallisation	Mixtures with difference in the solubility of the organic compound and its impurities in a solvent.	 Sugar with impurity of common salt can be crystallised from hot ethanol (sugar dissolves but salt does not). Benzoic acid and naphthalene from hot water (benzoic acid dissolves but naphthalene does not).
Sublimation	Mixtures of sublimable volatile compounds and non-sublimable impurities.	• Purification of camphor, anthracene, naphthalene, benzoic acid, etc.
Distillation	-	 Chloroform (b.pt. 334 K) and aniline (b.pt. 457 K). Ether (b.pt. 308 K) and toluene (b.pt. 383 K).
Fractional distillation		 Acetone (b.pt. 330 K) and methyl alcohol (b.pt. 338 K). Benzene (b.pt. 353 K) and toluene (b.pt. 383 K).



Steam distillation		 Purification of aniline (b.pt. 457 K). Nitrobenzene, <i>o</i>-nitrophenol, bromobenzene, etc.
Azeotropic distillation	Mixtures with constant boiling points-Azeotropic mixtures.	• Ethanol and water in ratio 95.87 : 4.13.
Vacuum distillation	Mixtures of high boiling liquids which decompose at or below their boiling points.	 Glycerol from spent-lye in soap industry (at 453 K under 12 mm Hg). Concentration of sugarcane juice.
Chromatography	Mixtures with difference in the rates at which the components of the mixture move through a porous medium.	·
Differential extraction	Mixtures of organic com- pounds from their aqueous solutions using a solvent that should (i) be immiscible with water, (ii) dissolve the organic compound.	• Benzoic acid from its water solution using benzene.

Qualitative Analysis

- □ An organic compound mainly consists of two elements carbon and hydrogen. In addition to these, it may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.
- The qualitative analysis of organic compounds involves the detection of all these major elements present in it with the help of suitable chemical tests.

Element	Detection	Confirmatory test	Reactions
Carbon	Copper oxide test $2CuO + C \xrightarrow{\Delta} 2Cu$ $+ CO_2^{\uparrow}$		$CO_2^{\uparrow} + Ca(OH)_2 \longrightarrow CaCO_3^{\downarrow} + H_2O$ Lime water Milkiness
Hydrogen		Water droplets appear on the cooler part of the ignition tube and also turns anhydrous $CuSO_4$ blue.	
Nitrogen	(L.E.) Na + C + N $\xrightarrow{\Delta}$	boil and cool + $FeCl_3$ + conc. HCl.	$\begin{array}{c} \operatorname{FeSO}_4 + 2\operatorname{NaOH} \longrightarrow \operatorname{Fe}(\operatorname{OH})_2 + \operatorname{Na}_2\operatorname{SO}_4 \\ \operatorname{Fe}(\operatorname{OH})_2 + 6\operatorname{NaCN} \longrightarrow \operatorname{Na}_4[\operatorname{Fe}(\operatorname{CN})_6] \\ + 2\operatorname{NaOH} \\ \operatorname{Na}_4[\operatorname{Fe}(\operatorname{CN})_6] + \operatorname{FeCl}_3 \xrightarrow{\operatorname{HCl}} \\ \operatorname{NaFe}[\operatorname{Fe}(\operatorname{CN})_6] + 3\operatorname{NaCl} \\ \operatorname{Prussian blue} \\ \operatorname{or } 3\operatorname{Na}_4[\operatorname{Fe}(\operatorname{CN})_6] + 4\operatorname{FeCl}_3 \\ \operatorname{Fe}_4[\operatorname{Fe}(\operatorname{CN})_6]_3 + 12\operatorname{NaCl} \\ \\ \operatorname{Prussian blue} \end{array}$

Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$ (L.E.)	 (i) L.E. + sodium nitroprusside. A deep violet colour. (ii) L.E. + CH₃COOH + (CH₃COO)₂Pb Gives a black ppt. 	(i) Na ₂ S + Na ₂ [Fe(CN) ₅ NO] \longrightarrow Sodium nitroprusside Na ₄ [Fe(CN) ₅ NOS] Deep violet (ii) Na ₂ S + (CH ₃ COO) ₂ Pb $\xrightarrow{CH_3COOH}$ PbS \downarrow + 2CH ₃ COONa Black ppt.
Halogens	$Na + X \xrightarrow{\Delta} NaX$ (L.E.)	 L.E. + HNO₃ + AgNO₃ (i) White ppt. soluble in aqueous NH₃ (or NH₄OH) confirms Cl. (ii) Yellow ppt. partially soluble in aqueous NH₃ (or NH₄OH) confirms Br. (iii) Yellow ppt. insoluble in aqueous NH₃ (or NH₄OH) confirms I. 	$NaX + AgNO_{3} \xrightarrow{HNO_{3}} AgX \downarrow$ $ppt.$ $AgCl \downarrow + 2NH_{3(aq.)} \longrightarrow [Ag(NH_{3})_{2}]Cl$ White ppt. Soluble
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta}$ NaSCN (L.E.) Sodium thiocyanate	-	NaSCN + FeCl ₃ → [Fe(SCN)]Cl ₂ + NaCl Blood red colour
Phosphorus	$P \xrightarrow{Na_2O_2, \text{ boil}}{\Delta} Na_3PO_4$		$Na_{3}PO_{4} + 3HNO_{3} \longrightarrow H_{3}PO_{4} + 3NaNO_{3}$ $H_{3}PO_{4} + 12(NH_{4})_{2}MoO_{4} + 21HNO_{3}$ $\longrightarrow (NH_{4})_{3}PO_{4} \cdot 12MoO_{3}\downarrow +$ Ammonium phosphomolybdate (Yellow ppt.) 21NH_{4}NO_{3} + 12H_{2}O

(1) KEY POINT

• Presence of oxygen in an organic compound can be detected indirectly by testing the compound containing functional group such as -OH, -CHO, $>C=O, -COOH, -NO_2, etc.$

Quantitative Analysis

The percentage composition of elements present in an organic compound is determined by the following methods :

Element	Method	Process	Formula
Carbon and Hydrogen	method	A known weight of the organic compound (<i>w</i> g) is combusted with excess of O ₂ and amount of CO ₂ and H ₂ O formed are used to determine percentage of C and H. $C_xH_y + \left(x + \frac{y}{4}\right)O_2 \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O$	(i) $C \longrightarrow CO_2$ 12 g 44 g $%C = \frac{12 \times \text{wt. of } CO_2 \times 100}{44 \times w}$ (ii) $2H \longrightarrow H_2O$ 2 g 18 g $%H = \frac{2 \times \text{wt. of } H_2O \times 100}{18 \times w}$



Nitrogen	(i)Dumas method (ii)Kjeldahl's method	Elemental nitrogen in organic compound (<i>w</i> g) is converted into molecular nitrogen by suitable chemical method and its volume is changed to S.T.P. data. $C_xH_yN_z + \left(2x + \frac{y}{2}\right)CuO \xrightarrow{\Delta}$ $xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$ Nitrogen in the organic compound (<i>w</i> g) is converted into NH ₃ by suitable chemical	$2N \longrightarrow N_{2(g)}$ $28 \text{ g} \qquad 22.4 \text{ L at S.T.P.}$ $\%N = \frac{28 \times V \times 100}{22.4 \times w}$ where V is the volume of N ₂ gas in L at S.T.P $2N \longrightarrow NH_3 \approx H_2SO_4$
		method which, in turn, is absorbed by V_1 mL of N_1 H ₂ SO ₄ . Organic compound $\xrightarrow{H_2SO_4} \xrightarrow{\Delta} (NH_4)_2$ SO ₄ $\xrightarrow{2NaOH} \Delta 2NH_3$ $\xrightarrow{H_2SO_4} (NH_4)_2$ SO ₄	$\%N = \frac{1.4 \times N_1 \times V_1}{w}$
Sulphur	Carius method	Sulphur in the organic compound (<i>w</i> g) is converted into H ₂ SO ₄ by boiling with conc. HNO ₃ and is precipitated as BaSO ₄ . $S \xrightarrow{(i) HNO_3, \Delta}_{(ii) BaCl_2} \xrightarrow{BaSO_4}_{white ppt.}$	$S \xrightarrow{g} H_2SO_4 \xrightarrow{g} BaSO_4$ $%S = \frac{32 \times \text{wt. of } BaSO_4 \times 100}{233 \times w}$
Halogen	Carius method	Halogen in the organic compound (w g) is precipitated as silver halide by boiling with conc. HNO ₃ and then adding AgNO _{3.}	(i) Cl \longrightarrow AgCl 35.5 g 143.5 g $%$ Cl = $\frac{35.5 \times \text{wt. of AgCl} \times 100}{143.5 \times w}$ (ii) Br \longrightarrow AgBr $^{80 \text{ g}}$ 188 g $%$ Br = $\frac{80 \times \text{wt. of AgBr} \times 100}{188 \times w}$ (iii) I \longrightarrow AgI $^{127 \text{ g}}$ 235 g $%$ I = $\frac{127 \times \text{wt. of AgI} \times 100}{235 \times w}$
Phosphorus	Ignition method	Phosphorus in organic compound (w g) is precipitated as magnesium ammonium phosphateby sequential reaction with nitric acid, MgCl ₂ and mixture of NH ₄ Cl + NH ₄ OH and then the precipitate is ignited to form magnesium pyrophosphate.	$Mg_2P_2O_7 \longrightarrow 2P$ $222 g 62 g$ $%P = \frac{\text{Mass of Phosphorus}}{\text{Mass of organic compound}} \times 100$ $= \frac{62 \times \text{wt.of } Mg_2P_2O_7 \times 100}{222 \times w}$
Oxygen			%O = 100 – Sum of the percentages of other elements

SELF CHECK

2.

1. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is (at. mass Ag =108; Br =80)

(a) 48 (b) 60)
---------------	---

(c) 24 (d) 36

(JEE Main 2015)

- 1.4 g of an organic compound was digested according to Kjeldahl's method and the ammonia evolved was absorbed in 60 mL of M/10 $\rm H_2SO_4$ solution. The excess sulphuric acid required 20 mL of M/10 NaOH solution for neutralisation. The percentage of nitrogen in the compound is
 - (a) 3 (b) 5
 - (d) 24 (c) 10

(JEE Main 2015)



Calculation of Empirical and Molecular Formula

- Empirical formula : It is the simplest whole number ratio between the atoms of the various elements present in one molecule of the substance.
- Molecular formula : It gives the actual number of atoms of each element present in one molecule of the substance.
- Molecular formula = n × Empirical formula where, n is an integer (1, 2, 3, etc.)

SOME BASIC PRINCIPLES OF ORGANIC CHEMISTRY

- Introduction
- Nomenclature
- Isomerism
- Electronic Displacement in a Covalent Bond
- Types of Organic Reactions

TIPS TO REMEMBER

- Berzelius, a Swedish chemist proposed that a 'vital force' is responsible for the formation of organic compounds.
- This was rejected by F. Wohler who synthesised first organic compound urea from an inorganic compound.

$$\begin{array}{ccc} \text{NH}_4\text{CNO} & \xrightarrow{\Delta} & \text{NH}_2\text{CONH}_2\\ \text{Ammonium cyanate} & & \text{Urea} \end{array}$$

Classification of Organic Compounds

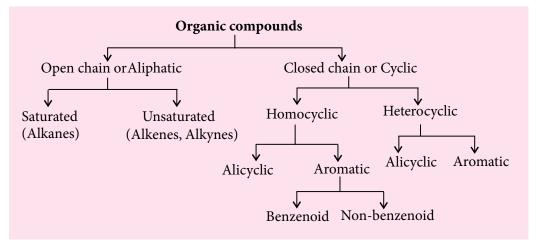
Based on structure :

- Acetic acid was synthesised by Kolbe and methane by Berthelot.
- Tetravalency of carbon : Carbon atom has four half filled orbitals in its excited state and hence forms four covalent bonds.
- **Shape and hybridisation :**

Hybridisa- tion	Structure and bond angle	Examples
sp ³	Tetrahedral, 109°28′	Ethane, methane
sp ²	Trigonal planar, 120°	Ethene, propene
sp	Linear, 180°	Ethyne, propyne

(1) KEY POINT

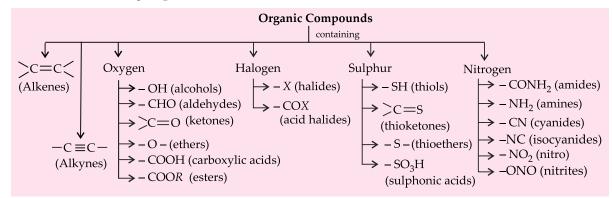
- Stability of a bond formed by a hybrid orbital is more than that formed by an unhybridised orbital.
- Greater the *s*-character of a hybrid orbital, lower is its energy. Hence the order of energies of various orbitals is $sp^3 > sp^2 > sp > s$.
- Greater the *s*-character of a hybrid orbital, smaller is its size. Therefore, the relative sizes of the hybrid orbitals follow the order $sp^3 > sp^2 > sp$.
- As expected from the size of the hybrid orbitals, *sp*-orbital forms the shortest and *sp*³ orbital forms the longest bond.



CHEMISTRY TODAY | DECEMBER '15

35

Based on functional groups :



Homologous Series

□ A series of organic compounds each containing a characteristic functional group forms a homologous series in which each successive member differs by a $-CH_2$ group or by $12 + 2 \times 1 = 14$ mass units.

The five parts are described as follows :

The members of the series are called homologues and the phenomenon is called *homology*.

IUPAC Nomenclature

□ IUPAC name = 2° prefix + 1° prefix + word root + 1° suffix + 2° suffix

Word root	1° prefix	2° prefix	1° suffix	2° suffix
It denotes the	It is used to differen-	Some functional	It is always added	It is added to indicate
number of carbon	tiate between	groups are not	to the word root to	a particular functional
atoms present in	cyclic and acyclic	considered as	indicate whether	group present in the
the principal chain	compounds.	functional groups	carbon chain	principal chain. e.g.,
of the compound.		but are treated as	is saturated or	alcohols, acids, acid
C_1 -meth, C_2 -eth,		substituents which	unsaturated.	derivatives etc.
C_3 -prop and C_4 -but.		are denoted by		
These are the special		secondary prefixes.		
names for first four		<i>e.g.</i> , Fluoro —F;		
carbons.		Chloro –Cl; Nitro		
		$-NO_2$		

IUPAC rules for nomenclature of hydrocarbons :

- Parent chain rule : From structure, the longest possible chain of C-atoms is chosen, this is called as parent chain. Accordingly, the appropriate root word is fixed.
- Lowest number rule : Once the parent chain is selected, the carbon atoms are numbered starting from the end that gives the lowest possible number to the carbon bearing substituent.
- Lowest set of locants rule : When more than one substituent is present, carbon atoms

bearing substituents should be numbered in such a way that there is least difference between them *i.e.*, that set of locants is preferred which has a lower number at the first point of difference.

- □ IUPAC nomenclature of compounds with polyfunctional groups :
 - If more than one functional groups are present then one functional group is treated as the principal functional group (secondary suffix) and the remaining functional groups are treated as substituents (prefixes).



Class	Group	Suffix	Prefix
		(if present	(if present as
		as a functional	a substituent)
		group)	
Carboxylic acids	—СООН	-oic acid	Carboxy
Sulphonic acids	—SO ₃ H	sulphonic acid	Sulpho
Esters	-COOR	alkyl alkanoate	Alkoxy carbonyl
Acyl halides	-COX	-oyl halide	Halocarbonyl
Amides	-CONH ₂	-amide	Carbamoyl
Nitriles	—C≡N	nitrile	Cyano
Isocyanides	-NC	isocyanide	Isocyano
Aldehydes	—СНО	-al	Formyl
Ketones	-CO	-one	Охо
Alcohols	-OH	-ol	Hydroxy
Thiols	—SH	-thiol	Sulphanyl
Amines	-NH ₂	amine	Amino
Imines	=NH	imine	Imino
Ethers	-0-	Alkoxy alkane	Alkoxy
Alkenes	>C=C<	-ene	Alkenyl
Alkynes	$-C \equiv C -$	-yne	Alkynyl
Halides	-X	_	Halo
Nitro	-NO ₂	_	Nitro
Alkanes		-ane	Alkyl

IUPAC nomenclature of aromatic compounds :

- For substituted benzene compounds, the substituent is placed as prefix to the word benzene.
- In disubstituted benzene ring, the substituents are located at the lowest numbers possible while numbering the carbon atoms of the ring.
- In the trivial system of nomenclature, the prefix *ortho* (*o*-) indicates 1,2-, *meta* (*m*-) indicates 1,3- and *para* (*p*-) indicates 1,4-disubstituted benzene ring.
- In case of tri- or higher substituted benzene derivatives, common name of benzene derivatives is taken as the base compound. Number 1 position is assigned to the substituent of the base compound and lowest locant rule is followed for other substituents.

• Benzene ring is considered as substituent [Phenyl (Ph), $-C_6H_5$] when it is attached to an alkane with a functional group.

1 KEY POINT

- Sometimes two equally long chains (but having different number of side chains) appear to be possible. In such cases, the chain which carries the larger number of side chains is the parent chain.
- Certain functional groups containing carbon as a part of the group (such as -CHO, -COOH, -COOR, -COCl and -CN) can be present only at one end of the chain. For such groups known as *chain terminating groups*, the numbering of the parent chain is always started from the carbon of this group. Therefore, such functional groups always get number 1 and this number need not be mentioned while writing the name of the compound.
- If the principal chain contains two or more multiple bonds, the numbering is done in accordance with lowest set of locants rule.



• If both double and triple bonds are present in the parent chain and numbering of parent chain from any end gives the same set of locants, then numbering is done from the end which gives the lowest locant to the double bond.

$$2$$
 3 4

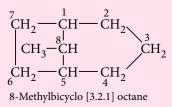
 Bicyclic compounds are named by adding prefix bicyclotothenameofhydrocarbon corresponding to total number of carbon atoms in two rings. In between the words bicyclo and alkane an expression in the square brackets is placed that represents the number of carbon atoms in each bridge connecting two bridge heads, in descending order separated from one another by full stop.

$$\begin{array}{c} CH_2-CH-CH_2\\ | & |\\ CH_2 & CH_2\\ | & |\\ CH_2-CH-CH_2\\ \end{array}$$

Bicyclo [3.2.1] octane

(1) KEY POINT

• If substituent is present, we number the bridged ring system beginning at one bridge head, proceeding first along the longest bridge to the other bridge head, then along the next longest bridge back to the first bridge head. The shortest bridge is numbered last.



Isomerism

□ The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as *isomerism*.

SELF CHECK

3. The number of optically active products obtained from the complete ozonolysis of the given compound is CH₂ H

CH₃-CH=CH-C-CH=CH-CH=CH-CH₃
$$\stackrel{\stackrel{i}{=}}{H}$$
 $\stackrel{\stackrel{i}{=}}{CH_3}$
(a) 0 (b) 1
(c) 2 (d) 4 (JEE Advanced 2012)

- 4. In allene (C₃H₄), the type(s) of hybridisation of the carbon atoms is(are)
 (a) sp and sp³
 (b) sp and sp²
 (c) only sp²
 (d) sp² and sp³
 (JEE Advanced 2012)
- Isomerism in an organic compound can be classified broadly into *structural* and *stereoisomerism*.

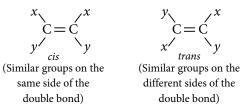
Isomerism	Description	Examples
Chain isomerism	Arises due to different arrangements of carbon atoms leading to linear and branched chains. The chain isomers have almost similar chemical properties but different physical properties.	CH ₃ H ₃ C-CH ₂ -CH ₂ -CH ₃ , H ₃ C-CH-CH ₃ Butane Iso-butane
Position isomerism	Arises due to different positions of side chains, substituents, functional groups, double bonds, triple bonds, etc. on the parent chain.	$H_2C = CH - CH_2 - CH_3,$ But-1-ene $H_3C - CH = CH - CH_3$ But-2-ene
Functional isomerism	Arises due to presence of different functional groups. The functional isomers have the same molecular formula but possess different functional groups. The functional isomers show different physical as well as chemical properties.	$H_3C - CH_2 - OH$, $H_3C - O - CH_3$ Ethyl alcohol Dimethyl ether
Metamerism	Arises when different alkyl groups are attached to the same functional group.	$\begin{split} H_{3}C - CH_{2} - O - CH_{2} - CH_{3} \\ & \text{Diethyl ether or Ethoxyethane} \\ H_{3}C - O - CH_{2} - CH_{2} - CH_{3} \\ & \text{Methyl propyl ether or 1-Methoxypropane} \end{split}$
Tautomerism	Refers to the dynamic equilibrium between two compounds with same molecular formula. It is also called as <i>desmotropism</i> or <i>kryptotropism</i> or <i>prototropy</i> or <i>allelo-tropism</i> . In general, the tautomers have different functional groups and exist in dynamic equilibrium with each other due to a rapid interconversion from one form to another.	$\begin{array}{cccc} O & OH \\ \parallel \\ H_3C - C - CH_3 & \rightleftharpoons & H_3C - C = CH_2 \\ Acetone & Prop-1-en-2-ol \\ (keto form) & (enol form) \\ Keto-enol tautomerism \\ O & (enol form) \\ H_3C - N & \bigoplus & H_2C = N \\ O & O \\ Nitromethane & (aci-form) \\ (nitro-form) \\ Nitro-aci tautomerism \end{array}$

38 CHEMISTRY TODAY | DECEMBER '15

Types of structural isomerism :

U Types of stereoisomerism :

• *Geometrical isomerism* : Geometrical isomers have the same structural formula but they differ in the spatial arrangement of atoms or groups of atoms about double bond (C = C, C = N or N = N).



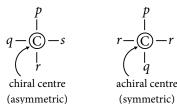
In addition to alkenes, compounds containing C=N (aldoxime and ketoxime) and N=N (azo compounds) bonds also show geometrical isomerism. However, in these cases, 'syn' (for cis) and 'anti' (for trans) are more commonly used.

$$\begin{array}{ccc} CH_{3 \ C} H & CH_{3 \ C} H \\ \parallel & \parallel \\ N \\ syn & aldoxime & HO \\ \end{array}$$

E and Z system of nomenclature : For highly substituted alkenes having four different atoms or groups attached to C = C bond, *cis* and *trans* designations cannot be used. In such cases, *E-Z* notation is used.

- *E* is assigned to an isomer in which high priority atoms or groups are on the opposite sides.
- *Z* is assigned to an isomer in which high priority atoms or groups are on the same side.
- In polyenes number of geometrical isomers = 2^n where, *n* is the number of double bonds.
- Optical isomerism : Compounds having similar physical and chemical properties but differing only in the behaviour towards polarised light are called optical isomers and the phenomenon is called optical isomerism.

- Some substances have the ability to rotate the plane polarised light either to the right (clockwise) or to the left (anticlockwise). These substances are termed as *optically active* substances and the property is called *optical activity*.
- In order to exhibit optical activity, an object must be *chiral*.
- The compound is said to have *chirality* if the central carbon atom is attached to four different groups and this centre is called *chiral (asymmetric) centre* or *stereogenic centre* or *stereocentre*.



- If molecule has a plane of symmetry it is *achiral* and if molecule has no plane of symmetry it is *chiral*.
- Enantiomers or d and l isomers are the optical isomers which are non-superimposable mirror images (or dissymmetric).
- Diastereomers are the optical isomers which are not mirror images of each other. They have different physical properties and magnitude of specific rotation.
- Meso compounds are those compounds which have two or more even number of chiral carbon atoms and have an internal plane of symmetry. They are optically inactive due to *internal compensation*.

I) KEY POINT

- Terminal alkenes like propene isobutylene,
 2, 3-dimethylbutene do not show geometrical isomerism.
- Geometrical isomers are also called configurational isomers as they have fixed configuration.
- Auwer Sketa Rule : This is an empirical rule according to which out of a pair of geometrical isomers (*cis* and *trans*) the *cis* isomers has higher b.pt., density and refractive index.

39

SELF CHECK

- 5. Which of the following compounds will exhibit geometrical isomerism?
 - (a) 2-Phenyl-1-butene
 - (b) 1, 1-Diphenyl-1-propane
 - (c) 1-Phenyl -2- butene
 - (d) 3-Phenyl-1-butene (JEE Main 2015)
- 6. Which of the following pairs of compounds are positional isomers?

(a)
$$CH_3-CH_2-CH_2-CH_2-CHO$$
 and
 O
 $CH_3-CH_2-CH_2-CH_3$

(b)
$$CH_3 - CH_2 - CH_2 - C-CH_3$$
 and
 U
 $CH_3 - CH - CH_2 - CHO$
 $CH_3 - CH - CH_2 - CHO$
 CH_3

(c)
$$CH_3 - CH_2 - CH_2 - CH_3$$
 and
 U
 $CH_3 - CH_2 - C - CH_3$ and
 $CH_3 - CH_2 - C - CH_2 - CH_3$

Reaction intermediates :

(d)
$$CH_3 - CH_2 - C - CH_2 - CH_3$$
 and
 H_0
(HEF Main

$$CH_{3}$$
 CH-CH₂-CHO (JEE Main 2015)
CH₃

7. The number of structural isomers for C_6H_{14} is

(JEE Main 2015)

Electronic Displacement in a Covalent Bond

Given Series : Fission of a covalent bond :

- *Heterolytic cleavage* involves breaking of a covalent bond in such a fashion that the shared pair of electrons remains with one of the fragments, which results in the formation of carbocations or carbanions as intermediates.
- Homolytic cleavage involves breaking of a covalent bond in such a fashion that one of the electrons of the shared pair goes with each of the bonded atom, which results in the formation of free radicals as intermediates.

Intermediates	Definition	Hybridisation of carbon and shape	Stability order
Carbocation	Carbon species carrying +ve charge on carbon.	sp^2 hybridised carbon and planar structure.	$3^{\circ} > 2^{\circ} > 1^{\circ}$
Carbanion	Carbon species carrying –ve charge on carbon.	<i>sp</i> ³ hybridised carbon and pyramidal shape.	$1^{\circ} > 2^{\circ} > 3^{\circ}$
Free radical	Atom or group of atoms having odd or unpaired electron.	sp^2 hybridised carbon and planar structure.	$3^{\circ} > 2^{\circ} > 1^{\circ}$

□ Attacking reagents :

Reagent	Description	Examples
Electrophiles	They are positively charged or neutral molecules having electron deficient atom, seeking a site of high electron density. Electrophiles have an incomplete outer shell and are also called <i>Lewis</i> <i>acids</i> (electron-pair acceptors).	$X = \text{Cl, Br, I}, \text{ NO}_{2}^{+}, \text{ NO}_{4}^{+}, \text{ SO}_{3}\text{H}, \text{ C}_{6}\text{H}_{5}\text{N}_{2}^{+}, \text{ NH}_{4}^{+}, \text{ SO}_{3}\text{H}, \text{ C}_{6}\text{H}_{5}\text{N}_{2}^{+}, \text{ NH}_{4}^{+}, \text{ SO}_{4}\text{H}, \text{ C}_{6}\text{H}_{5}\text{N}_{2}^{+}, \text{ NH}_{4}^{+}, \text{ SO}_{4}\text{H}, \text{ C}_{6}\text{H}_{5}\text{H}_{5}^{+}, \text{ NH}_{4}^{+}, \text{ SO}_{4}\text{H}, \text{ C}_{6}\text{H}_{5}\text{H}_{2}^{+}, \text{ NH}_{4}^{+}, \text{ SO}_{4}\text{H}, \text{ C}_{6}\text{H}_{5}\text{H}_{2}^{+}, \text{ NH}_{4}^{+}, \text{ SO}_{4}\text{H}, \text{ NH}_{4}^{+}, \text{ SO}_{4}\text{H}, \text{ C}_{6}\text{H}_{5}\text{H}_{2}^{+}, \text{ NH}_{4}^{+}, \text{ SO}_{4}\text{H}, \text{ NH}_{4}^{+}, \text{ SO}_{6}\text{H}_{5}\text{H}_{5}^{+}, \text{ NH}_{6}^{+}, \text$

Nucleophiles	They are negatively charged or neutral molecules having electron-rich atom with unshared electron pair, seeking electron deficient site to attack. They are also called <i>Lewis bases</i> (electron-pair donors).	CN, N ₃ , RO, R, RS, SH, HSO ₃ , NO ₂ , NH ₂ ,
Ambiphiles (ambidents)	They behave like both electrophiles and nucleophiles hence, have dual nature (amphoteric).	

- **D** Electron displacement effects in covalent bonds :
 - Inductive effect : Displacement of σ electrons 0 along a saturated carbon chain when an electron donating (+I effect) or electron withdrawing (-I effect) group is attached at the end of the carbon chain.
 - Decreasing order of -I effect : $-NO_2 >$ -CN > -COOH > -F > -Cl > -Br >-I > -H
 - Decreasing order of +I effect : $(CH_3)_3C^{--}$ $> (CH_3)_2CH \rightarrow CH_3CH_2 \rightarrow CH_3 \rightarrow CH$ $D \rightarrow H$
 - *Electromeric effect* : It involves complete transfer of π electrons of a multiple bond towards one of the bonded atoms in the presence of an attacking reagent.
 - +E effect: When electron transfer takes place towards the atom to which the attacking reagent gets attached.
 - -*E* effect : When electron transfer takes place away from the atom to which the attacking reagent gets attached.
 - Resonance or Mesomeric effect : It is defined as 0 the polarity produced in the molecule by the interaction of two π bonds or between a π bond and a lone pair of electrons present on adjacent atom.
 - +*R* or +*M* effect : -OH, -OR, -SH, -SR, $-NH_2$, -NHR, $-NR_2$, -Cl, -Br, -I, etc.
 - -R or -M effect : >C = O, -CHO,-COOR, -CN, $-NO_2$, etc.
 - Hyperconjugation : It involves delocalisation 0 of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p*-orbital. For an alkyl group attached to unsaturated system it decreases with decrease in number of α -hydrogens :

$$CH_3 \rightarrow CH_3CH_2 \rightarrow (CH_3)_2CH \rightarrow (CH_3)_3C \rightarrow CH_3 \rightarrow CH_3CH_2 \rightarrow (CH_3)_3C \rightarrow CH_3CH_2 \rightarrow CH_3CH_3 \rightarrow CH_3 \rightarrow C$$

Types of Organic Reactions

- Substitution reactions (or displacement reactions) : These are further classified into three types :
 - 0 Free radical substitution reaction takes place through free radical intermediates, e.g.,

$$CH_4 + Cl_2 \frac{h\upsilon}{\text{or } 670 \text{ K}} CH_3 Cl + HCl$$

(Here, Cl[•] is formed as reaction intermediate)

- *Electrophilic substitution reaction* (S_E) involves 0 the attack by an electrophile. It is of two types :
 - Unimolecular (S_E 1) is first order reaction. _ These reactions are very rare and generally takes place in aliphatic compounds, e.g., $CH_3CH_2MgBr + HBr \longrightarrow CH_3CH_3 +$ Ν

Bimolecular (S_{E2}) is second order reaction and very common in aromatic compounds where π -electrons of benzene ring are highly delocalised and an electrophile can attack this region of high electron density.

$$\bigcirc + CH_3Cl \xrightarrow{AlCl_3} \bigcirc + HCl$$

0 Nucleophilic substitution reactions (S_N) are those reactions in which a stronger nucleophile displaces a weaker nucleophile and the atom or group which departs with its bonding pair of electrons is called the *leaving* group (or nucleofuge).

$$\overset{\delta^+}{\underset{\text{Substrate Nucleophile}}{\overset{\delta^-}{\underset{\text{Substrate Nucleophile}}{\overset{\delta^+}{\underset{\text{Substrate Nucleophile}}{\overset{\delta^+}{\underset{\text{Substrate Nucleophile}}}} R - \text{Nu} + X^-_{\text{Leaving group}}$$

Unimolecular (S _N 1)	Bimolecular (S _N 2)
It is first order reaction.	It is second order reaction.
Generally carried out in polar protic solvents like water, alcohol and acetic acid.	-
Takes place in two steps through carbocation as the intermediate.	Takes place in one step through transition state.
Rate of reaction : $3^{\circ} > 2^{\circ} > 1^{\circ} > CH_3$ (fastest) (slowest) Greater the stability of carbocation, faster will be the reaction.	$\begin{array}{l} \text{Rate of reaction:} \\ \text{CH}_3 > 1^\circ > 2^\circ > 3^\circ \text{ halides} \\ \text{(fastest)} \qquad (\text{slowest)} \\ \text{Lesser the steric hindrance} \\ \text{in transition state, faster} \\ \text{will be the reaction.} \end{array}$
weak nucleophiles	Tends to proceed with strong nucleophiles, <i>e.g.</i> ; CH_3O^- , CN^- , OH^- , etc.
•	Inversion of configuration takes place (<i>Walden</i> <i>inversion</i>).

- Better the leaving group, more facile is the reaction. It is of two types :

Addition reactions :

$$H_2C = CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2 - CH_2Br$$

These are also of three types like substitution reactions : Electrophilic addition, Nucleophilic addition and Free radical addition reactions.

Elimination reactions : These are opposite of addition reactions in which two atoms or groups of atoms are lost to form compounds with double and triple bonds, *e.g.*;

$$CH_3CH_2OH \xrightarrow{conc. H_2SO_4} CH_2 = CH_2 + H_2O$$

- These are of three types : Unimolecular elimination (E1), Unimolecular conjugate base elimination (E1cb) and Bimolecular elimination (E2) reactions.
- Rearrangement reactions : These reactions involve reorganisation of the constituent parts of a molecule. In these, functional groups, double bonds, H atoms or alkyl groups are moved from one C atom to another, *e.g.*;

42

$$(CH_3)_3C - CH = CH_2 \xrightarrow{Acid}_{catalyst}$$

 $(CH_3)_2C = C(CH_3)_2$
Wöhler synthesis :

$$\begin{array}{ccc} \text{NH}_4\text{CNO} & \xrightarrow{\text{Heat}} & \text{NH}_2\text{CONH}_2 \\ \text{Ammonium cyanate} & & \text{Urea} \end{array}$$

• Beckmann rearrangement :

$$CH_{3} \xrightarrow{PCl_{5}} CH_{3} \xrightarrow{O} \underset{||}{CH_{3}-C=NOH} \xrightarrow{PCl_{5}} CH_{3} \xrightarrow{O} C-NHCH_{3}$$
Acetoxime N-Methylacetamide

1 KEY POINT

0

• Relative stabilities of carbocations follow the order :

– benzylic ~
$$3^{\circ}$$
 > allylic ~ 2° > 1° > CH_3

• Relative stabilities of carbanions follow the order : aromatic > benzyl > allyl > HC $\equiv \bar{C}$ > H₂C $\equiv \bar{C}$ H

$$>\overline{CH}_3 > CH_3\overline{CH}_2 > (CH_3)_2\overline{CH} > (CH_3)_3\overline{C}$$

 $1^\circ \qquad 2^\circ \qquad 3^\circ$

• Relative stabilities of free radicals follow the order :

$$C_{6}H_{5}\dot{C}H_{2} > CH_{2} = CH\dot{C}H_{2} > (CH_{3})_{3}\dot{C} >$$
(Benzyl) (Allyl) 3°
(CH_{3})_{2}\dot{C}H > CH_{3}\dot{C}H_{2} > \dot{C}H
2° 1°

SELF CHECK

8. The order of stability of the following carbocations is

$$CH_{2} = CH_{I} - CH_{2}; CH_{3} - CH_{2} - CH_{2}; \bigcup_{II}$$
(a) III > I > II (b) III > II > I
(c) II > III > I (d) I > II > III
(b) III > II > III

(JEE Main 2013)

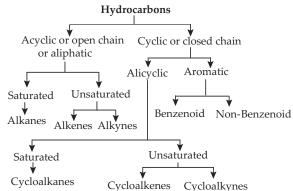
HYDROCARBONS

- - Alkenes
 - Alkynes
 - Aromatic Hydrocarbons

TIPS TO REMEMBER

 Organic compounds composed of only carbon and hydrogen are called *hydrocarbons*.

Classification

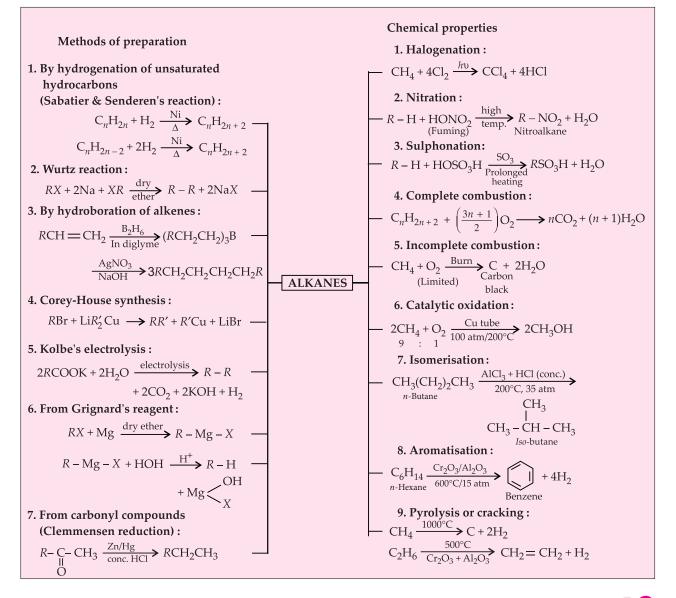


Alkanes

□ The saturated hydrocarbons are represented by the general formula C_nH_{2n+2} .

General properties :

- The normal alkanes are colourless gases $(C_1 \text{ to } C_4)$, colourless liquids $(C_5 \text{ to } C_{17})$ and from C_{18} onwards colourless solids.
- As branching increases, melting and boiling points decrease. The boiling point increases steadily with increase in molecular mass.
- Density of alkanes also increases with size of the molecule.
- They are generally insoluble in polar solvents like water but soluble in non-polar solvents like ether, chloroform, etc.



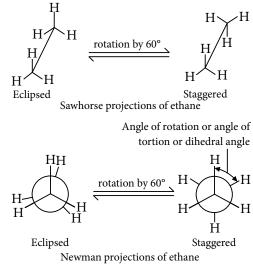
CHEMISTRY TODAY | DECEMBER '15

 Mechanism of halogenation : The mechanism is believed to involve the following steps :

$$\begin{array}{l} \operatorname{Cl}_{2} \longrightarrow \operatorname{Cl}^{1} + \operatorname{Cl}^{1} (\operatorname{Initiation \ step}) \\ \operatorname{Cl}^{1} + \operatorname{CH}_{4} \longrightarrow \operatorname{CH}_{3} + \operatorname{HCl} \\ \operatorname{CH}_{3} + \operatorname{Cl}_{2} \longrightarrow \operatorname{CH}_{3} \operatorname{Cl}^{1} + \operatorname{Cl}^{*} \\ \operatorname{Cl}^{1} + \operatorname{Cl}^{1} \longrightarrow \operatorname{Cl}^{-} \operatorname{Cl} \\ \operatorname{Cl}^{1} + \operatorname{Cl}^{1} \longrightarrow \operatorname{Cl}^{-} \operatorname{Cl}_{3} \operatorname{Cl}^{2} \\ \operatorname{CH}_{3} + \operatorname{Cl}^{*} \longrightarrow \operatorname{CH}_{3} \operatorname{Cl}^{2} \\ \end{array} \right\} (\operatorname{Termination \ step}) \\ \begin{array}{c} \operatorname{Reactivity} \ of \ halogens : \operatorname{F}_{2} > \operatorname{Cl}_{2} > \operatorname{Br}_{2} > \operatorname{I}_{2} \\ \operatorname{Reactivity} \ of \ hydrogen : \operatorname{3}^{\circ} > \operatorname{2}^{\circ} > \operatorname{1}^{\circ} \end{array} \right)$$

- Conformations of Ethane (Sawhorse and Newman Projections)
 - Staggered conformation : The hydrogen atoms attached to two carbons are far apart and experience minimum repulsion.
 - *Eclipsed conformation* : The hydrogen atoms attached to two carbons are as close together as possible and experience maximum repulsion.
 - Gauche or Skew form : A rotation of 60° converts a staggered conformation into an eclipsed conformation, or vice-versa. Rotation between 0° to 60° generates one of the many other arrangements in between staggered and eclipsed forms. These arrangements are called gauche or skew form.
 - Order of stability :





🕦 KEY POINT

44

- Methane cannot be prepared by Kolbe's electrolytic method.
- Ethane is prepared in the laboratory by electrolysis of conc. aqueous solution of CH₃COOK.

1) KEY POINT

- Electrolysis of HCOONa gives H₂ gas at both cathode as well as anode.
- During chlorination the relative ease of abstraction of H atom is 1: 3.8 : 5 for primary, secondary and tertiary hydrogen respectively.
- In bromination the ratio becomes 1 : 82 : 1600 for 1°, 2° and 3° H atoms. The yield of alkanes produced can be accordingly predicted.

SELF CHECK

9. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.

$$I\left[\begin{array}{c} \downarrow \\ \downarrow \\ and \\ \downarrow \end{array}\right] II\left[\begin{array}{c} \downarrow \\ and \\ \downarrow \end{array}\right]$$
$$III\left[\begin{array}{c} \downarrow \\ and \\ \downarrow \end{array}\right]$$

The correct order of their boiling point is

(a) I > II > III (b) III > II > I

(c)
$$II > III > I$$
 (d) $III > I > II$

(JEE Advanced 2014)

10. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO₂. The empirical formula of the hydrocarbon is

(a)
$$C_7H_8$$
 (b) C_2H_4
(c) C_3H_4 (d) C_6H_5

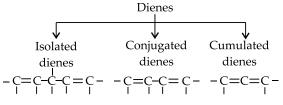
(JEE Main 2013)

- 11. Which branched chain isomer of the hydrocarbon with molecular mass 72 u gives only one isomer of mono substituted alkyl halide?
 - (a) Neopentane (b) Isohexane
 - (c) Neohexane (d) Tertiary butyl chloride

(JEE Main 2012)

Alkenes

Organic compounds containing C = C are known as *alkenes*. Alkenes with two double bonds are known as *dienes*.



- □ Methods of preparation :
 - *By dehydration of alcohols :*

$$\begin{array}{c} \begin{array}{c} - \begin{array}{c} C \\ - \end{array} \\ - \begin{array}{c} C \\ - \end{array} \\ - \begin{array}{c} C \\ - \end{array} \\ - \begin{array}{c} D \\ - \end{array} \end{array} \xrightarrow{95\% H_2 SO_4} \\ \Delta \end{array} > C = C <$$

Saytzeff rule : If a single starting compound can yield two or more isomers then more substituted alkene is formed in greater amount.

• By dehydrohalogenation of alkyl halides :

$$- \overset{l}{\underset{H}{\overset{\circ}{\xrightarrow{}}}} \overset{l}{\underset{\Lambda}{\overset{\circ}{\xrightarrow{}}}} \overset{l}{\xrightarrow{}} \overset{l}{\xrightarrow{}$$

• Partial hydrogenation of alkynes :

$$- R - C \equiv C - R + H_2 \xrightarrow{Pd/CaCO_3} H_{Cis-Alkene} R = C = C < R + H_2$$

Birch reduction :

$$R - C \equiv C - R \xrightarrow{\text{Na/Liq. NH}_3} H C = C < H_{\text{trans-Alkene}}$$

• Electrolysis of salt of dicarboxylic acids :

$$\begin{array}{c} CH_2COONa \xrightarrow{Electro} CH_2COO^{-} \\ | \\ CH_2COONa \xrightarrow{} | \\ CH_2COO^{-} \end{array} \xrightarrow{} \begin{array}{c} CH_2 \\ | \\ CH_2COO^{-} \end{array} \xrightarrow{} \begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} + 2CO_2 \end{array}$$

• *Hofmann elimination :*

$$(C_2H_5)_4 NOH^{-} \xrightarrow{heat} (C_2H_5)_3 N + CH_2 = CH_2$$

Tetraethyl ammonium
hydroxide $+ H_2O$

• Wittig reaction :

$$\begin{array}{c} R \\ H \end{array} \subset = O + (C_6H_5)_3P = CH_2 \xrightarrow{\text{heat}} \\ Methylene triphenyl \\ phosphorus \\ R - CH = CH_2 + (C_6H_5)_3P = O \end{array}$$

$$H_2O_2 \text{ or } \mathbb{P}$$

• Cope reaction :
$$R_3N \xrightarrow{CF_3COOH} R_3N - O$$

3°-Amine $R_3N - O$
3°-N-oxide

Properties :

- All alkenes are colourless and odourless (except ethene). Ethene has pleasant odour.
- $C_1 C_3$ (gases), $C_4 C_{16}$ (liquids), C_{17} onwards solids.
- Boiling point, melting point and specific densities increase with increase in molecular mass in homologous series.

• *Mechanism of electrophilic addition : Step 1 :* The reagent ionises

$$E \stackrel{f}{\longrightarrow} Nu \longrightarrow E^{\oplus} + :Nu^{\oplus}$$

$$Step \ 2 : E^{\oplus} + \stackrel{f}{\longrightarrow} E^{\oplus} = C \stackrel{f}{\longrightarrow} \stackrel{f}{\longrightarrow$$

 $CH_2 = CH_2 > R - CH = CH_2 > R_2C = CH_2 \approx R - CH = CH - R > R_2C = CHR > R_2C = CR_2$

- *Markovnikov's rule* : The negative part of unsymmetrical reagent adds to less hydrogenated carbon atom of double bond.
- Peroxide effect : Addition of HBr in presence of peroxide gives products opposite to Markovnikov's rule.

$$CH_{3} - CH = CH_{2} + HBr$$

$$Markovnikov's rule$$

$$H_{2}O_{2}$$

$$(Peroxide effect)$$

$$CH_{3}CHBrCH_{3}$$

$$CH_{3}CH_{2}CH_{2}Br$$

• Oxymercuration-demercuration :

$$R - CH = CH_2 \xrightarrow{Hg(OAc)_2}_{THF/H_2O} R - CH - CH_2HgOAc$$
$$OH$$
$$\xrightarrow{NaBH_4/NaOH} R - CH - CH_3$$
$$OH$$

• Ozonolysis :

• Polymerisation :

$$nCH_2 = CH_2 \xrightarrow{473 \text{ K}}_{O_2} (CH_2 - CH_2)_n$$

 Oxidation : Hot alkaline KMnO₄ or K₂Cr₂O₇ as oxidising agent

$$C = C \begin{pmatrix} \frac{\text{hot KMnO}_4}{\Delta} \\ C = C \begin{pmatrix} -C \\ 0H \end{pmatrix} \\ (OH) \\ (O$$

iranchembook.ir/edu

CONCEPT MAP

SUB-ATOMIC

PARTICLES AND

ATOMIC MODELS

STRUCTURE OF ATOM

Electrons

• Negatively charged

• Charge = -1.6022×10^{-19} C

• Mass = 9.10939×10^{-31} kg

• Relative charge = -1

material particles.

Thomson

Model

• An atom has a spherical shape

in which the positive charge is

uniformly distributed and electrons

• Explained overall neutrality of the atom but could not explain

> the results of scattering experiments

are embedded.

Nearly all properties of matter can be explained in terms of atoms consisting of electrons, protons and neutrons and the various models given to describe the structure of atom are based on classical, quantum and wave mechanical concepts.

Protons

• Positively charged material particles. • Charge = $+1.6022 \times 10^{-19}$ C • Mass = 1.67262×10^{-27} kg • Relative charge = +1

SUB-ATOMIC

PARTICLES

ATOMIC

MODELS

QUANTUM

NUMBERS

A set of four numbers which gives

complete information

about an electron.

Rutherford's

Model

• An atom consists of a small

positively charged nucleus and

• Could not explain the stability of

atom, line spectra of elements,

distribution of electrons and

energies of electrons.

electrons revolve around it.

Neutrons

• Electrically neutral particles. • Charge = 0• Mass = 1.67493×10^{-27} kg

Bohr's Model

- Electrons revolve around the nucleus in certain definite orbits called stationary states having fixed energies.
- Electrons revolve only in those orbits for which the angular momentum is an integral multiple of $\frac{h}{2\pi}$
- Radii of stationary states, $r_n = \frac{a_0 n^2}{Z}$ Energies of different stationary states, $E_n = \frac{-1312}{n^2} Z^2 \text{ kJ mol}^{-1}$
- Velocity of electrons in n^{th} orbit, $v_n = 2.188 \times 10^8 \times \frac{Z}{n}$ cm s⁻¹
 - No. of spectral lines = $\frac{(n_2 n_1)(n_2 n_1 + 1)}{2}$
 - Applicable only for one electron system. • Does not explain Zeeman and Stark effects.

ELECTRO-MAGNETIC RADIATIONS

Wave Nature of Electromagnetic Radiations

• Electrically charged particle under acceleration produces electromagnetic waves.

$c = \upsilon \lambda$ and $\frac{1}{\lambda} = \overline{\upsilon}$

• Electromagnetic spectrum : Cosmic rays < γ-rays < X-rays < UV rays < Visible < Infrared < Micro waves < Radio waves (Increasing order of wavelength).

of Electromagnetic Radiations • Particle nature explains the following

Particle Nature

phenomena:

- Black body radiation : Radiation emitted by a black body.

- *Photoelectric effect* : Emission of electrons from the surface of a metal when radiation of certain minimum frequency strikes the metal and the kinetic energy of ejected electron,

 $\frac{1}{2}mv^2 = hv - hv_0$

Quantum **Mechanical Model**

• Based on the following two concepts : Heisenberg's uncertainty principle : The exact position and exact momentum of an electron cannot be determined simultaneously. $\Delta x \times \Delta p \ge \frac{h}{1}$

- Dual behaviour of matter : All material particles possess wave as well as particle character and the wave associated with a particle is called de-Broglie wave.

 $\lambda = \frac{h}{mv} = \frac{h}{p}$

Principal Quantum Number (n)

• Tells size and energy of an orbital.

Maximum number of electrons in a shell is given by $2n^2$.

Spin Quantum Number (s or m_s) • Tells direction of electron spin and has value +1/2 or -1/2.

Magnetic Quantum Number (*m*_l)

• Tells number of orbitals present in any subshell. • For a given value of *l*, it can have

all the values ranging from -l to +l including zero.

Azimuthal Quantum Number (/)

• Tells number of subshells and shape of

orbitals. • For a particular value of *n*, l = 0 to (n - 1)• Shape of *s*-orbital is spherical, *p*-orbital is dumb-bell and that of d- orbital is double dumb-

bell.

(1) KEY POINT

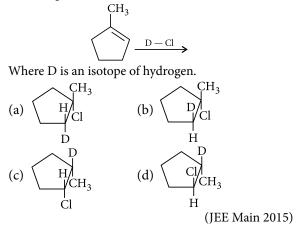
- In case of dialkyl derivatives of ethylene which exist as geometrical isomers, the *trans* isomer is more stable than the *cis* isomer. This is because of lesser crowding in trans isomers.
- With alkaline KMnO₄, = CH₂ part of alkene is oxidised to CO₂ and H₂O = CRR' part is oxidised to RCOR'
- N-Bromosuccinimide (NBS) is used for the bromination of alkenes at allylic position.
- RhCl(Ph₃P)₃ is Wilkinson's catalyst and used for the hydrogenation of alkenes.

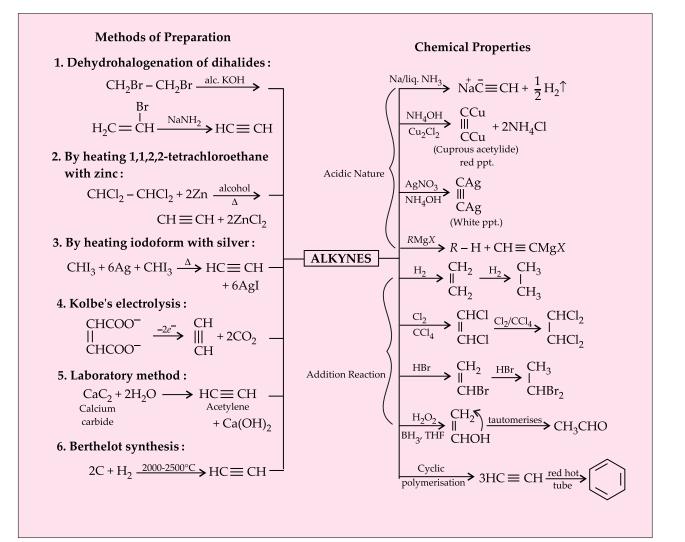
Alkynes

 \Box Hydrocarbons with $C \equiv C$ are known as *alkynes*.

SELF CHECK

12. What is the major product expected from the following reaction?







• Acidic nature : Acetylene is acidic in nature. As *s*-character increases, acidic nature increases.

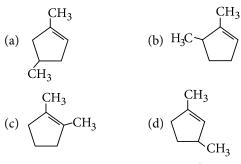
```
Hybridisation : sp > sp^2 > sp^3 (acidic nature)
s-character : 50% 33.3% 25%
```

1 KEY POINT

- Alkaline KMnO₄ (MnO₄ + OH⁻) is known as Baeyer's reagent and used for test of unsaturation (glycol forms).
- Alkynes show chain, position and functional isomerism.
- Acetylene can undergo linear polymerisation by passing it through CH₂Cl₂ solution containing NH₄Cl. (Monovinyl acetylene and divinyl acetylene are formed).

SELF CHECK

13. Which compound would give 5-keto-2-methyl-hexanal upon ozonolysis?



(JEE Main 2015)

Aromatic Hydrocarbons

Given Structure of benzene :

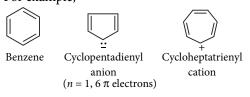
- All six carbon atoms in benzene are sp^2 hybridised.
- The sp^2 hybrid orbitals overlap with each other and with *s*-orbitals of the six hydrogen atoms forming C – C and C – H σ bonds respectively.

Chemical properties :

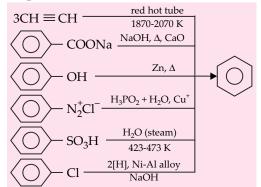
- All σ-bonds in benzene lie in one plane and all bond angles are 120°.
- One half of π-molecular orbital lies above and the other half lies below the plane of the σ-bond.

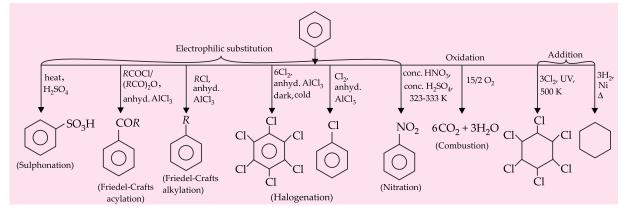


- Aromaticity (Huckel Rule) : Huckel rule of aromaticity is applied to all the ring systems whether they have benzene ring or not and possess the following characteristics :
 - Planarity
 - Complete delocalisation of π -electrons in the ring.
 - Presence of $(4n + 2)\pi$ -electrons in the ring where n = 0, 1, 2, 3, ...For example,



D Preparation :





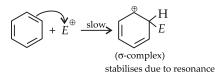
CHEMISTRY TODAY | DECEMBER '15

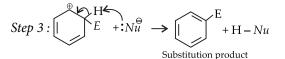
 Mechanism of electrophilic substitution reactions: Benzene undergoes substitution because it is an electron rich system due to delocalised π-electrons.

Step 1 : Formation of an electrophile

$$E \stackrel{f}{-} \stackrel{\checkmark}{Nu} \longrightarrow E^{\oplus} + : Nu^{\ominus}$$

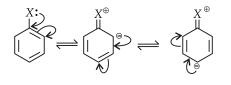
Step 2 : Electrophile attacks on aromatic ring to form σ -complex.





Directive influence :

• Groups with positive mesomeric effect (+*M*) increases electron density at *o*- and *p*-positions due to delocalisation.



(here *X* may be – OH, – F, – Cl, – Br, – I.)

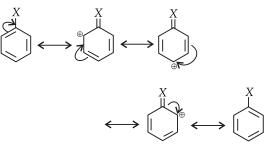
Thus, electrophile attacks on *o*- and *p*-positions because these are electron rich positions while nucleophile will attack on *m*-position because *m*-position is less electron rich.

ORGANIC COMPOUNDS CONTAINING HALOGENS

- Preparations, Properties and Reactions
- Nature of C X bond

50

 Uses and Environmental Effects of Chloroform, Iodoform, Freons and DDT

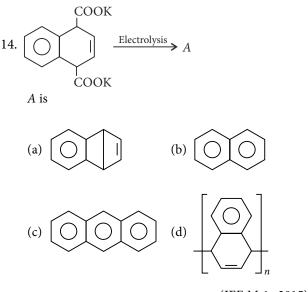


(here, $X \text{ may be} - \text{NO}_2$, $- \text{SO}_3\text{H}$, - CN.)

1) KEY POINT

- *o*, *p*-directing groups also activate benzene ring towards further substitution while *meta*-directing groups deactivate benzene ring.
- Halogens are exception; they are *o*, *p*-directing but deactivating.

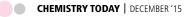
SELF CHECK

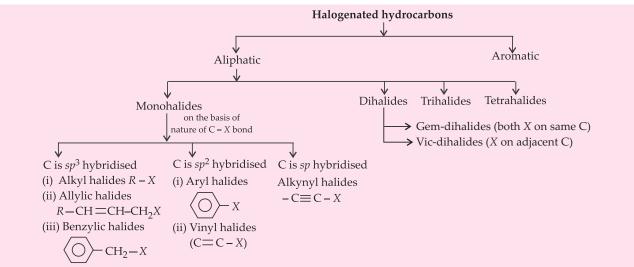


(JEE Main 2015)

TIPS TO REMEMBER

 Halogen derivatives are derived from hydrocarbons by the replacement of one or more hydrogen atoms with halogens.





Aliphatic halogen derivatives

Methods of preparation :

$$RCH_{2}OH + HX \xrightarrow{ZnCl_{2}} -H_{2}O$$

$$RCH_{2}OH + PX_{5} \xrightarrow{-POX_{3}} -HX$$

$$RCH_{2}OH + SOX_{2} \xrightarrow{pyridine} -SO_{2}$$

$$RCH_{2}COOAg + X_{2} \xrightarrow{CCl_{4}}$$

$$(Hunsdiecker reaction)$$

$$RCH_{2}Cl + NaX \xrightarrow{Acetone}$$

$$(Finkelstein reaction)$$

Nature of C - X bond : C - X bond is highly polarised because X is more electronegative than C. Thus, haloalkanes are highly reactive towards nucleophilic substitution reactions.

$$\geq C^{\delta^+} X^{\delta^-}$$

- Order of reactivity : 0 C - F < C - Cl < C - Br < C - I
- Order of bond length : 0 C - F < C - Cl < C - Br < C - I
- Order of bond enthalpy : \mathbf{O} C - F > C - Cl > C - Br > C - I
- Order of dipole moment : 0 C - Cl > C - F > C - Br > C - I
- Haloarenes are less reactive towards nucleophilic 0 substitution reactions than haloalkanes. This low reactivity can be attributed to the following factors:
 - The C—X bond in halobenzene has a partial double bond character due to involvement

of halogen electrons in resonance with benzene ring.

The C—X bond in aryl halides is less polar as compared to that in alkyl halides as sp^2 hybridised carbon is more electronegative than sp^3 hybridised carbon.

Mechanism of substitution reaction :

 $S_N 2$ reaction : The mechanism is a one step concerted mechanism in which attack of nucleophile and the displacement of the halide ions take place simultaneously.

$$HO \xrightarrow{H} C \xrightarrow{Br} H \xrightarrow{\delta} \begin{bmatrix} \delta \xrightarrow{H} & H \\ HO \xrightarrow{I} & C \xrightarrow{H} \\ HO \xrightarrow{I} & H \\ H \end{bmatrix}$$

$$Transition state$$

$$\downarrow HO \xrightarrow{H} HO \xrightarrow{I} H = F$$

- Order of reactivity towards $S_N 2$ reaction : $CH_3 - X > CH_3CH_2 - X > (CH_3)_2CH - X >$ $(CH_3)_3C - X$
- Rate of S_N2 reaction depends upon the concentration of halide and nucleophile both so it is called *bimolecular nucleophilic* substitution. S_N2 reaction proceeds through inversion of configuration.
- $S_N 1$ reaction : Mechanism involves two steps : 0

First step: $R_3C - X \xrightarrow{\text{slow}} R_3C^+ + X^-$ Second step :

$$R_3C^+ + :Nu^- \xrightarrow{fast} R_3C - Nu$$

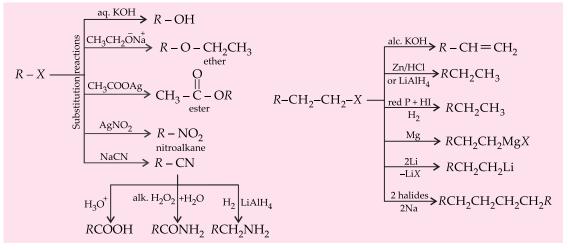
CHEMISTRY TODAY | DECEMBER '15 51



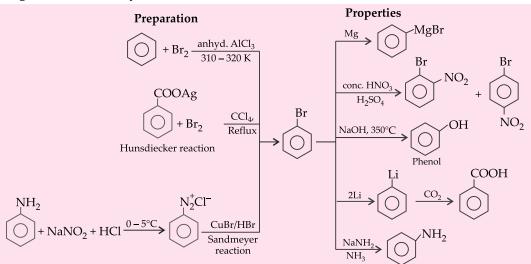
So, rate depends only upon the concentration of halide because it is only participating in slow or rate determining step.

- Reactivity order:
$$(CH_3)_3C - X > (CH_3)_2CHX$$

> $CH_3CH_2X > CH_3 - X$



Aromatic halogen derivatives (Aryl halides)



1 KEY POINT

- Direct iodination is not possible as it is a reversible reaction hence, it is carried out in presence of an oxidising agent like HIO₃ or HNO₃.
- The presence of electron withdrawing groups like –NO₂, –CN, –COOH etc., in *ortho* and *para* positions makes the halogen atom easily replaceable while the presence of electron releasing groups like –NH₂, –OH, –OR etc. decreases the reactivity.

SELF CHECK

- 15. The synthesis of alkyl fluorides is best accomplished by
 - (a) Finkelstein reaction (b) Swart's reaction
 - (c) free radical fluorination
 - (d) Sandmeyer's reaction. (JEE Main 2015)

- 16. The major organic compound formed by the reaction of 1,1,1-trichloroethane with silver powder is
 - (a) 2-butene (b) acetylene
 - (c) ethene (d) 2-butyne

(JEE Main 2014)

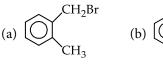
17. In S_N^2 reactions, the correct order of reactivity for the following compounds :

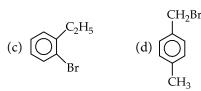
CH₃Cl, CH₃CH₂Cl, (CH₃)₂CHCl and (CH₃)₃CCl is

- (a) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$
- (b) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$
- (c) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
- (d) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$ (JEE Main 2014)

52 CHEMISTRY TODAY | DECEMBER '15

18. Compound (A), C_8H_9Br , gives a white precipitate when warmed with alcoholic AgNO₃. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A).





(JEE Main 2013)

CH₂Br

Compounds	Uses	Effects
Chloroform (CHCl ₃)	• Its major use is in the production of Freon refrigerant, R-22.	chloride, known as phosgene.
	• It is used as a solvent for resins, rubbers, oils and fats, alkaloids, iodine and many other substances.	$2CHCl_3 + O_2 \xrightarrow{\text{Light}} 2COCl_2 + 2HCl$ Phosgene gas causes liver and kidney damage.
	• In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage.	O Inhaling chloroform vanours depresses
	• It is used in preparation of chloretone (drug) and chloropicrin (insecticide).	
	• It is used to preserve anatomical species.	
Iodoform (CHI ₃)	• It is used as an antiseptic in dressing of wounds due to liberation of iodine.	• It has strong smell.
	• It is used as methylating agent in organic synthesis.	
Freons	• They are used as refrigerants, blowing agents, propellants in medical applications and degreasing solvent.	• Freons cause disruption of ozone layer by initiating radical chain reactions in stratosphere.
		• This anthropogenic compound is a green-house gas and its effect is more than CO_2 .
DDT	• In 1940, it was used as a pesticide.	• It is a persistent organic pollutant, strongly absorbed by soil.
		• It is lipophilic so has a high potential to bioaccumulate.
		• It may be directly genotoxic but may also induce enzymes to produce other genotoxic intermediates and DNA adducts.

(1) KEY POINT

- Iodoform has antiseptic properties because on coming in contact with organic matter of skin it decomposes to give free iodine which is an antiseptic.
- Before using the sample of chloroform as an anaesthetic it is tested by treating with aqueous solution of AgNO₃. A pure sample does not give precipitate with AgNO₃.

ANSWER KEYS (SELF CHECK)									
1.	(c)	2.	(c)	3.	(a)	4.	(b)	5.	(c)
6.	(c)	7.	(c)	8.	(a)	9.	(b)	10.	(a)
11.	(a)	12.	(b)	13.	(d)	14.	(b)	15.	(b)
16.	(d)	17.	(c)	18.	(a)				



Exam **Café**

QUESTIONS FOR PRACTICE

- 1. There are several criteria of purity of organic compounds. Which is considered to be the best?
 - (a) Melting point (b) Mixed melting point
 - (c) Colour
 - (d) Microscopic examination
- The most satisfactory method of separating sugars 2. from each other is
 - (a) fractional crystallisation
 - (b) sublimation
 - (c) chromatography
 - (d) distillation.
- 3. Azeotropes are
 - (a) liquid mixtures, which distil unchanged in composition
 - (b) liquids mixed in equal proportions
 - (c) solids which form solutions of definite composition
 - (d) gaseous mixtures, which cannot be separated.
- 4. Liquids which decompose below their normal boiling points can be distilled at lower temperature by
 - (a) increasing the pressure
 - (b) decreasing the pressure
 - (c) heating in water bath
 - (d) heating in sand bath.
- In a Lassaigne's test for sulphur in the organic 5. compound with sodium nitroprusside solution the violet colour formed is due to
 - (a) $Na_4[Fe(CN)_5NOS]$
 - (b) $Na_3[Fe(CN)_5S]$
 - (c) Na₂[Fe(CN)₅NOS]
 - (d) $Na_3[Fe(CN)_6]$
- In Lassaigne's test sodium metal is used because (a) it is very reactive
 - (b) its melting point is low
 - (c) its compounds are soluble in water
 - (d) all of the above.
- 7. In the estimation of nitrogen by Dumas method 1.18 g of an organic compound gave 224 mL of N₂ at STP. The percentage of nitrogen in the compound is about

(a)	20.0	(b)	11.8
(c)	47.5	(d)	23.7

CHEMISTRY TODAY | DECEMBER '15

- 8. Which of the following statements is incorrect?
 - (a) Using Lassaigne's test, nitrogen and sulphur present in an organic compound can be tested.
 - (b) Using Beilstein's test, the presence of halogens in a compound can be tested.
 - (c) In Lassaigne's filtrate, the nitrogen in an organic compound is converted to NaCN.
 - (d) In the estimation of carbon, an organic compound is heated with CaO in a combustion tube.
- 9. The IUPAC name of

$$CH_3CH = CHCH_2CHCH_2COOH$$
 is

- (a) 5-aminohept-2-enoic acid
- (b) β -amino- δ -heptanoic acid
- (c) 5-aminohex-2-enecarboxylic acid
- (d) 3-aminohept-5-enoic acid.
- **10.** Among the following carbocations,
 - Ph₂CCH₂Me (I)
 - (II) PhCH₂CH₂CHPh
 - (III) Ph₂CHĊHMe
 - (IV) $Ph_2C(Me)\dot{C}H_2$
 - the order of stability is
 - (a) IV > II > I > III(b) I > II > III > IV
 - (c) II > I > IV > III(d) I > IV > III > II
- 11. The enol form of acetone after treatment with D_2O gives

(a)
$$CH_3 - C = CH_2$$
 (b) $CH_3 - C - CD_3$

(c)
$$CH_2 = C - CH_2D$$
 (d) $CD_2 = C - CD_3$

- **12.** Allylic bromination of an olefin is
 - (a) nucleophilic substitution
 - (b) electrophilic substitution
 - (c) free radical substitution
 - (d) electrophilic addition.
- 13. The strongest base among the following is
 - (a) NH_4^+ (b) : NH₃ (c) NH_2^- (d) OH⁻



- 14. What is the relationship between keto and enol tautomers?
 - (a) Resonance forms
 - (b) Constitutional isomers
 - (c) Stereoisomers
 - (d) Different conformations of the same compound
- **15.** In the following reaction, the product '*R*' is

$$\operatorname{CaC}_2 \xrightarrow{\operatorname{H}_2 O} P \xrightarrow{\operatorname{hot iron}} Q \xrightarrow{\operatorname{CH}_3 Cl} R$$

- (a) benzene (b) ethylbenzene
- (c) toluene (d) *n*-propylbenzene. ¹COOH

16. In the compound H-— OH configurations — H HOare

- 4¹ COOH (a) *R*, *R* (b) *R*, *S* (c) *S*, *R* (d) *S*, *S*
- 17. In presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov's addition to alkenes because
 - (a) both are highly ionic
 - (b) one is oxidising and the other is reducing
 - (c) one of the steps is endothermic in both cases
 - (d) all steps are exothermic in both cases.
- **18.** An alkane C_7H_{16} is produced by the reaction of lithium di-3-pentylcuprate with ethyl bromide. The structural formula of product is
 - (a) 3-methylhexane
 - (b) 2-ethylpentane
 - (c) 3-ethylpentane
 - (d) *n*-heptane.
- 19. Using AlCl₃ and HCl as catalyst, which one of the following reactions produces ethylbenzene?
 - (a) $H_3C CH_2OH + C_6H_6$
 - (b) $CH_3 CH = CH_2 + C_6H_6$
 - (c) $H_2C = CH_2 + C_6H_6$
 - (d) $H_3C CH_3 + C_6H_6$
- **20.** The compound $X(C_5H_8)$ reacts with ammoniacal AgNO₃ to give a white precipitate, and on oxidation with hot alkaline KMnO₄ gives the acid, $(CH_3)_2$ CHCOOH. Therefore, X is
 - (a) $CH_2 = CHCH = CHCH_3$
 - (b) $CH_3(CH_2)_2C \equiv CH$
 - (c) $(CH_3)_2CH C \equiv CH$
 - (d) $(CH_3)_2C = C = CH_2$

21. A hydrocarbon of formula C_6H_{10} absorbs only one molecule of H_2 upon catalytic hydrogenation. Upon ozonolysis the hydrocarbon yields

The hydrocarbon is

- (a) cyclohexane (b) benzene
- (c) cyclohexene (d) cyclobutane.
- 22. Ethoxyethane and methoxypropane are
 - (a) geometrical isomers
 - (b) optical isomers
 - (c) functional group isomers
 - (d) metamers.
- 23. When neo-pentyl bromide is subjected to Wurtz reaction, the product formed is
 - (a) 2,2,4,4-tetramethylhexane
 - (b) 2,2,4,4-tetramethylpentane
 - (c) 2,2,5,5-tetramethylhexane
 - (d) 2,2,3,3-tetramethylhexane.
- 24. The product formed during the reaction is $CH \equiv CH + NaOCl \xrightarrow{0^{\circ}C}$
 - (a) 1,2-dichloroethane (b) 1,2-dichloroethenal
 - (c) 1,2-dichloroethene (d) 1,2-dichloroethyne.
- 25. 1-Chlorobutane on reaction with alcoholic potash gives
 - (b) 1-butanol (a) 1-butene
 - (c) 2-butene (d) 2-butanol.
- 26. Iodoform when treated with silver powder forms
 - (a) methane (b) ethane
 - (c) ethene (d) ethyne.
- 27. An alkyl chloride (A) produces a single alkene on reaction with sodium ethoxide and ethanol. The alkene further undergoes hydrogenation to yield 2-methylbutane. The alkyl chloride (A) is
 - (a) $ClCH_2C(CH_3)_3$
 - (b) ClCH₂CH₂CH₂CH₃
 - (c) ClCH₂CH(CH₃)CH₂CH₃
 - (d) CH₃C(Cl)(CH₃)CH₂CH₃
- 28. Which of the following is the best scientific method to test presence of water in a liquid?
 - (a) Smell
 - (b) Taste
 - (c) Use of litmus paper
 - (d) Use of anhydrous copper sulphate

CHEMISTRY TODAY | DECEMBER '15 55



- **29.** A sample of chloroform before being used as an anaesthetic is tested by
 - (a) AgNO₃ solution
 - (b) AgNO₃ solution after boiling with alc. KOH
 - (c) Fehling's solution
 - (d) ammoniacal Cu_2Cl_2 .
- **30.** Toluene on reaction with *N*-bromosuccinimide gives
 - (a) *p*-bromomethylbenzene
 - (b) o-bromomethylbenzene
 - (c) phenylbromomethane
 - (d) *m*-bromomethylbenzene.

SOLUTIONS

- 1. (b): Mixed melting point is considered to be the best criteria for purity of a substance. The purified sample is mixed with a small quantity of pure compound and melting point of mixture is determined. If melting point of mixture is same as that of the pure compound, the sample compound is pure, otherwise it requires further purification.
- 2. (c) : Best method to separate many components from a mixture is chromatography.
- **3.** (a): Azeotropes are constant boiling liquid mixtures which distil without any change in composition.
- **4.** (b): By decreasing the pressure, their boiling points can be lowered.
- 5. (a):

 $Na_2S + Na_2[Fe(CN)_5(NO)] \longrightarrow Na_4[Fe(CN)_5NOS]$ (From Lassaigne's Sodium extract) nitroprusside Sodium thionitroprusside (Violet colour)

- 6. (d): Sodium metal fulfills all the requirements.
- 7. (d): Percentage of nitrogen

$$= \frac{28}{22400} \times \frac{\text{Volume of N}_2 \text{ at STP}}{\text{Weight of organic compound}} \times 100$$

$$=\frac{28}{22400}\times\frac{224}{1.18}\times100=23.73\%$$

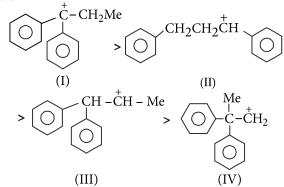
8. (d): In the estimation of carbon, organic compound is heated with excess of oxygen and CuO.

9. (d):
$$\overset{7}{CH}_{3} - \overset{6}{CH} = \overset{5}{CH} - \overset{4}{CH}_{2} - \overset{3}{CH} - \overset{2}{CH}_{2} - \overset{1}{COOH}_{1}$$

NH₂
3-Aminohept-5-enoic acid

CHEMISTRY TODAY | DECEMBER '15

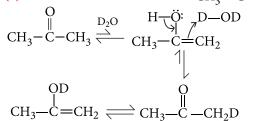
10. (b):



Stability of carbocations depends upon the number of resonating structures and the extent of +I, and -I effects.



```
11. (a): The enol form of acetone is CH_3 - C = CH_2.
```



- **12.** (c) : It is a free radical substitution reaction.
- **13.** (c) : Conjugate acid of NH₂⁻*i.e.*, NH₃ is the weakest acid among the given compounds, thus, NH₂⁻ is the strongest base.
- 14. (b): Keto-enol tautomers have same molecular formula but different functional groups and exist in dynamic equilibrium with each other hence, they are constitutional isomers.

15. (c) :
$$CaC_{2} + 2H_{2}O \longrightarrow HC \equiv CH + Ca(OH)_{2}$$

Calcium
carbide
 (P)
 $3CH \equiv CH \xrightarrow{Hot iron tube}_{873 K} \bigoplus_{Benzene}^{(Q)}_{Benzene}$
 (Q)
 $ightarrow CH_{3}Cl \longrightarrow_{O} CH_{3}$
 $ightarrow Benzene$
 (Q)
 $ightarrow CH_{3}Cl \longrightarrow_{O} Benzene$
 (Q)
 (Q)



17. (c) : The reaction of HCl with carbon radical in case of HCl, and addition of iodine radical to double bond in case of HI are endothermic steps.

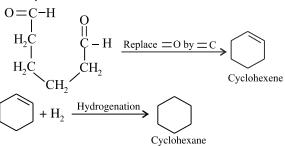
18. (c) :

$$CH_3$$

 CH_2
 $(CH_3-CH_2-CH-)_2CuLi + C_2H_5Br$
 CH_3
 $CH_3 - CH_2-CH-Cu$
 $CH_3 - CH_2 - CH-Cu$
 $CH_2 + CH_2 + LiBr$
 $CH_3-CH_2-CH-C_2H_5$
 3 -Ethylpentane
19. (c) :

$$CH_2 = CH_2 \xrightarrow{H^+, AlCl_3} CH_3 - \overset{+}{CH_2} \xrightarrow{C_6H_6} C_6H_5C_2H_5$$

- 20. (c) : Since the compound X (C₅H₈) reacts with ammoniacal AgNO₃ to give a white precipitate, it must be a terminal alkyne, *i.e.*, it should have $-C \equiv CH$ group. Further, since X gives (CH₃)₂CHCOOH on oxidation, X must have (CH₃)₂CHC $\equiv C -$ group. Thus, the compound X is (CH₃)₂CHC \equiv CH.
- 21. (c) : The parent alkene can be obtained by replacing = 0 by = C.



22. (d): Metamers differ in nature of alkyl groups on either side of the functional group.

23. (c):

$$CH_{3} \qquad CH_{3} \qquad CH_{3} \qquad H_{3}C - C - CH_{2}Br + 2Na + Br - CH_{2} - C - CH_{3} \xrightarrow{\text{ether}} CH_{3} \qquad CH_{3} \qquad CH_{3} \qquad CH_{3} \qquad CH_{3} \qquad H_{3}C - C - CH_{2} - CH_{2} - CH_{2} - CH_{3} \qquad H_{3}C - C - CH_{2} - CH_{2} - CH_{3} \qquad H_{3}C - C - CH_{3} \qquad CH$$

24. (d): With NaOCl, acetylene undergoes substitution in the absence of light.

 $HC \equiv CH + 2NaOCI \xrightarrow{0^{\circ}C} CI - C \equiv C - CI + 2NaOH$

58

25. (a) : Alkyl halides, on treatment with strong base like alc. KOH, undergo elimination reaction rather than substitution reaction.

$$ClCH_2 - CH_2 - CH_2 - CH_3 \xrightarrow{alc.KOH} \\ 1-Chlorobutane \\ CH_2 = CH - CH_2 - CH_3 \\ But-1-ene \\ CH_2 = CH - CH_2 - CH_3 \\ But-1-ene \\ CH_2 = CH - CH_2 - CH_3 \\ CH_2 = CH - CH_2 - CH_3 \\ CH_2 = CH - CH_2 - CH_3 \\ CH_2 = CH_3 \\ CH_3 \\ CH_3 = CH_3 \\ CH_3$$

26. (d): Ethyne (HC \equiv CH) is formed.

$$CH[I_3 + 6Ag + I_3]CH \xrightarrow{\Delta} HC \equiv CH + 6AgI$$

Ethyne

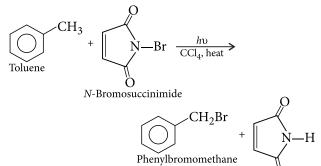
$$CICH_{2} - CH_{-}CH_{2} - CH_{3} \xrightarrow{\underset{C_{2}H_{3}OH}{C_{2}H_{3}OH}} CH_{2} = C - CH_{2} - CH_{3}$$

$$CH_{3} \xrightarrow{\underset{C}{}H_{2}} CH_{3} \xrightarrow{\underset{C}{}H_{2}} CH_{3} \xrightarrow{\underset{C}{}H_{2}} CH_{3} \xrightarrow{\underset{C}{}CH_{3}} CH_{3} \xrightarrow{\underset{C}{}CH_{3}} CH_{3} \xrightarrow{}CH_{3} \xrightarrow{}CH_{3$$

28. (d): Hydrated $CuSO_4$ is blue in colour, while anhydrous is white.

$$CuSO_4 + 5H_2O \longrightarrow CuSO_4.5H_2O$$
White
Blue

- **29.** (a) : A sample of chloroform before being used as an anaesthetic is tested by treating with aqueous solution of AgNO₃. A pure sample does not give precipitate with aqueous AgNO₃.
- **30.** (c) : Allylic bromination takes place by NBS (free-radical reaction).

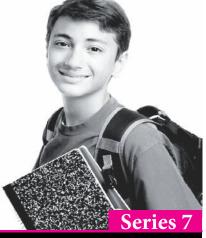




Attempt free online test and analyse your performance

Log on to http://test.pcmbtoday.com





CHAPTERWISE PRACTICE PAPER : ALDEHYDES, KETONES AND CARBOXYLIC ACIDS | AMINES

Time Allowed : 3 hours

Maximum Marks: 70

GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- (v) Q. no. 23 is a value based question and carries 4 marks.
- (vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.
- 1. Which type of aldehydes undergo Cannizzaro reaction?
- 2. How is acetone obtained from 2-bromopropane?
- 3. What is esterification?

 $N(CH_3)_2$

- **4.** Write down the IUPAC name of
- 5. What is the order of basicity of 1°, 2° and 3° ethyl substituted amines in aqueous solution?
- 6. An organic compound 'A' with molecular formula $C_5H_8O_2$ is reduced to *n*-pentane on treatment with Zn-Hg/HCl. 'A' forms a dioxime with hydroxylamine and gives a positive iodoform and Tollens' test. Identify the compound 'A' and deduce its structure.
- 7. Which acid of each pair shown here would you expect to be stronger?
 - (i) CH_3CO_2H or CH_2FCO_2H (ii) F_3C \longrightarrow COOH or H_3C \longrightarrow COOH

OR

- Carboxylic acids are higher boiling liquids as compared to corresponding aldehydes, ketones or alcohols. Explain.
- (ii) What happens when primary alcohols are oxidised by potassium permanganate?
- 8. (i) When propanone is subjected to Wolff Kishner reduction, what product will be obtained? Give chemical equation.
 - (ii) How will you convert acetaldehyde to acetone?
- 9. Mention two important uses of sulphanilic acid.
- **10. (i)** Which amino compounds are used as surfactants?
 - (ii) What is the order of boiling points of isomeric amines?
- **11.** Write the reactions with conditions for the following conversions :
 - (i) Methanal to propan-1-ol
 - (ii) Benzaldehyde to benzyl alcohol
 - (iii) Benzaldehyde to benzophenone

CHEMISTRY TODAY | DECEMBER '15

- 12. Explain the following observations :
 - (i) In aqueous solution the K_b order is $Me_2NH > MeNH_2 > Me_3N$
 - (ii) The diazonium ion acts as an electrophile.
 - (iii) Tertiary amines do not undergo acylation reaction.
- **13. (i)** How will you convert :
 - (a) Propanone to propan-2-ol.
 - (b) Propanone to 2-methyl-2-propanol.

(Write the reaction and state the reaction conditions in each case.)

- (ii) Write a distinction test for acetaldehyde and acetone.
- Carboxylic acids are more acidic than phenols. 14. (i) Why?
 - (ii) The carboxylic carbon is less electrophilic than carbonyl carbon. Explain.
- How will you convert : 15. (i)
 - (a) Benzene into aniline
 - (b) 3-Methylaniline into 3-nitrotoluene
 - (ii) Give one chemical test to distinguish between aniline and N-methylaniline.

OR

- (a) Account for the following : **(i)** Like ammonia, amines good are nucleophiles.
 - (b) Aryl amines are weaker bases than alkyl amines.
- (ii) Predict the product of the following reaction : NH₂

$$\frac{1}{Cu, \Delta} \xrightarrow{\text{NaNO}_2/\text{HBF}_4}$$

- 16. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents :
 - (i) PhMgBr and then H_3O^+
 - (ii) Semicarbazide and weak acid
 - (iii) Excess of ethanol and dry hydrogen chloride gas
- Describe the following giving a chemical 17. (i) equation for each :
 - (a) Cannizzaro reaction
 - (b) Trans-esterification
 - (ii) Account for the following : Electrophilic substitution in benzoic acid takes place at meta-position.

- **18.** Explain the following :
 - tert-Butylbenzene does not give benzoic (i) acid on oxidation with acidic KMnO₄. Give reasons.
 - (ii) The carbonyl oxygen atom of a carboxylic acid is more basic than hydroxyl oxygen.
- An organic compound 'A' having molecular 19. (i) formula C₂H₇N on treatment with HNO₂ gave an oily yellow substance. Identify 'A'.
 - (ii) How are 1°, 2° and 3°-amines distinguished?
- **20.** (i) Identify the substances '*A*' and '*B*'.

- (ii) Why is benzenediazonium chloride not stored and is used immediately after its preparation?
- (iii) Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?
- 21. (i) Explain the mechanism of the following reaction : Addition of Grignard reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.
 - (ii) Write the structure of 4-chloropentan-2-one.
 - (iii) Name the products formed on oxidation of 2, 5-dimethylhexan-3-one.
- Arrange the following compounds in increasing 22. (i) order of their reactivity in nucleophilic addition reactions.
 - (a) Ethanal, Propanal, Propanone, Butanone.
 - (b) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.
 - (ii) Give plausible explanation for the following : During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.
- 23. During the chemistry practical in laboratory, Piyush removed labels from the bottles of acetaldehyde and acetone to irritate lab assistants. His classmate, Abhishek who noticed his act told him that he should not play with the chemicals like this as it could be dangerous for us.
 - (i) What values are shown by Abhishek?
 - (ii) How can these chemicals be distinguished for correct labelling?
 - (iii) Name two methods which are commonly used to convert C=O group present in acetaldehyde and acetone into a CH_2 group.
 - (iv) Write two uses of acetone.





24. Compound 'A' $(C_6H_{12}O_2)$ on reduction with LiAlH₄ yields two compounds 'B' and 'C'. The compound 'B' on oxidation gives 'D' which on treatment with aqueous alkali and subsequent heating furnishes 'E'. The latter on catalytic hydrogenation gives 'C'. The compound 'D' on further oxidation gives CH₃COOH. Deduce the structures of *A*, *B*, *C*, *D* and *E*.

OR

- **(i)** What happens when
 - (a) malonic acid is heated with urea in presence of POCl₃
 - (b) ethanal reacts with air in presence of cobalt acetate?
- (ii) Illustrate the following name reactions :
 - (a) Cross aldol condensation
 - (b) Hell-Volhard-Zelinsky reaction
- 25. (i) How can you prepare monobromoaniline from aniline?
 - (ii) Explain the following :
 - (a) Coupling reaction of a diazonium salt.
 - (b) Aqueous ethylamine turns red litmus blue.
 - (c) Methylamine in water reacts with ferric chloride to precipitate ferric hydroxide.

OR

- (i) Although amino group is o, p-directing in aromatic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
- (ii) How will you prepare the following compounds from benzenediazonium chloride :
 - (a) Benzene (b) A yellow dye
 - (c) An orange dye?
- 26. (i) Addition of ammonia derivatives to carbonyl compound takes place in weakly acidic medium (pH = 3.5) only. Why?
 - (ii) Carbonyl carbon is an electrophilic whereas carbonyl oxygen is a nucleophilic centre. Why?
 - (iii) How are formalin and trioxane related to methanal?

OR

An aromatic compound 'A' (C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollens' or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' ($C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction. Identify A, *B* and *C* and write all the reactions involved.

SOLUTIONS

Those aldehydes which do not have an α -hydrogen, 1. undergo Cannizzaro reaction. e.g., HCHO, C₆H₅CHO.

2.
$$CH_3-CH-CH_3 \xrightarrow{aq. KOH} CH_3-CH-CH_3$$

2-Bromopropane $CH_3-CH-CH_3$
 $Cu \downarrow 573 K$
 O
 $CH_3-CH-CH_3$
 $Cu \downarrow 573 K$
 O
 CH_3-C-CH_3
 $CH_3-CH-CH_3$

Carboxylic acids on reaction with alcohols or phenols in the presence of a mineral acid such as conc. H₂SO₄ or HCl gas form ester. This reaction is called esterification reaction.

$$\begin{array}{ccc} RCOOH & + R'OH & \stackrel{H'}{\longrightarrow} RCOOR' + H_2O \\ Carboxylic Acid & Alcohol & Ester & Water \\ \end{array}$$

- 4. *N*,*N*-Dimethylbenzenamine
- 5. Order of basicity of ethyl substituted amines is : $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$ due to steric hindrance to H-bonding, +I effect predominates.
- 6. **(i)** The organic compound 'A' $(C_5H_8O_2)$ is reduced to n-pentane on treatment with Zn-Hg/HCl and gives positive iodoform test. Hence, it may be an aldehyde or ketone containing chain of 5-carbon atoms.
 - (ii) Since it gives positive Tollens' test, it must be an aldehyde.
 - (iii) It forms dioxime with hydroxylamine therefore, it contains two aldehydic groups.

- 7. (i) H_2 CFCOOH will be stronger of the two. The presence of electronegative F-atom at the α -C causes electron withdrawal from the -COOH and facilitates the release of H⁺.
 - (ii) $F_3C \rightarrow \bigcirc \bigcirc \bigcirc$ COOH is more acidic due to the presence of electron withdrawing -CF₃ group in it.

CHEMISTRY TODAY | DECEMBER '15 61



OR

- (i) Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses due to more extensive association of carboxylic acid molecules by intermolecular hydrogen bonding.
- (ii) Primary alcohols on oxidation with potassium permanganate give carboxylic acids.

8. (i)
$$CH_3 - C - CH_3 \xrightarrow{NH_2 - NH_2} alc. KOH \rightarrow CH_3 - CH_2 - CH_3 + N_2$$

Propanone $CH_3 - CH_2 - CH_3 + N_2$
Propane
(ii) $CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow{Ca(OH)_2} -CO_2, -H_2O} \rightarrow CH_3COOH \xrightarrow{Ca(OH)_2} -CO_2, -H_2O} \rightarrow CH_3 - CH_3 - CH_3 - CH_3 - CH_3 - CCO_3 (CH_3COO)_2Ca$

- **9.** (i) Sulphanilic acid is used in the manufacture of dyes.
 - (ii) It is used in the preparation of sulpha drugs such as sulphathiazole, sulphapyridine, etc.
- **10. (i)** Quaternary ammonium salts are used as surfactants.
 - (ii) The order of boiling points of isomeric amines is primary > secondary > tertiary. H

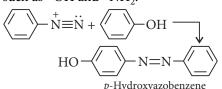
11. (i)
$$H-C=O + CH_3CH_2MgBr \xrightarrow{Dry ether}$$

Methanal Grignard reagent H_2O/H^+ $H_1 - C-OMgBr$
Propan-1-ol $H_1 - C-OMgBr$
Propan-1-ol H_2OH
 $H_1 - C-OMgBr$
 CH_2CH_3 H_2CH_3
 $H_3CH_2CH_2OH + CH_2OH$
(ii) H_2CH_3
Benzaldehyde H_2OH
(iii) $C_6H_5CHO \xrightarrow{Reduction}_{Ni + H_2} \bigoplus_{Benzyl alcohol}$
(iii) $C_6H_5CHO \xrightarrow{K_2Cr_2O_7}_{H_2SO_4} C_6H_5COOH \xrightarrow{Ca(OH)_2}_{Benzaldehyde}$
 $C_6H_5-CO-C_6H_5 \xrightarrow{Dry distillation}_{-CaCO_3} (C_6H_5COO)_2Ca$
Benzophenone

CHEMISTRY TODAY | DECEMBER '15

62

- 12. (i) In alkyl amines, a combination of +I effect of alkyl groups, steric factors and H-bonding factors determine the stability of ammonium cations in aqueous solution. All these factors are favourable for 2° amines and for smaller $-CH_3$ group, stability due to hydrogen bonding predominates over the stability due to +I effect. Consequently, we get the given K_b order : $Me_2NH > MeNH_2 > Me_3N$
 - (ii) The diazonium ion is electrophile because there is positive charge on terminal nitrogen. It can react with nucleophilic aromatic compound (Ar H) activated by electron donating groups such as -OH and -NH₂.



(iii) Tertiary amines do not undergo acylation reaction because they do not contain any H-atom on the nitrogen atom.

1

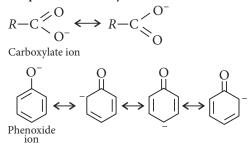
3. (i) (a)
$$CH_3 \\ CH_3 \\ Propanone \\ CH_3 \\ CH_3$$

(ii) Acetaldehyde reduces Tollens' reagent to silver mirror while acetone does not.

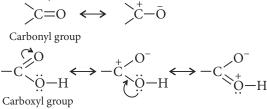
CH₃CHO + 2[Ag(NH₃)₂]⁺ + 3OH⁻ → CH₃COO⁻ + 2H₂O + 2Ag↓ + 4NH₃ CH₃COCH₃ + Tollens' reagent → No reaction

14. (i) The higher acidity of carboxylic acid as compared to phenol is due to the stabilisation of carboxylate ion by two resonating structures in which -ve charge is at the more electronegative oxygen. But in resonating structures of phenoxide ion the -ve charge is at less electronegative carbon atom. So,

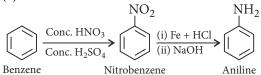
resonance stabilisation in phenoxide ion is less as compared to carboxylate ion.



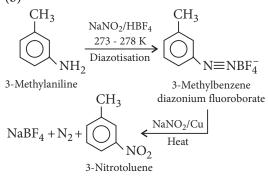
(ii) Due to resonating structures of carboxylate ion, carboxylic carbon is less electrophilic than carbonyl carbon.



15. (i) (a)



(b)

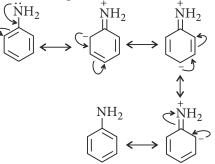


(ii) Aniline and *N*-methylaniline can be distinguished by carbylamine test. Aniline, the primary amine on heating with chloroform in presence of alcoholic KOH forms isocyanide having unpleasant smell.

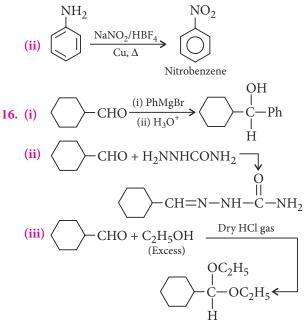
$$NH_{2}$$
+ CHCl₃ + 3KOH_(alc.)
+ CHCl₃ + 3KOH_(alc.)
- N \geq C + 3KCl + 3H₂O
Isocyanide

OR

- (a) Amines like ammonia (i) are good nucleophiles. This is because alkyl group in an amine shows electron releasing effect. This increases the electron density on 'N' of amino group and hence, makes the amines very good nucleophiles.
 - (b) Due to resonance in aniline, the lone pair of electrons on nitrogen gets delocalised over the benzene ring and becomes less available for protonation.



In alkyl amine, alkyl group releases electrons and increases electron density on nitrogen, making it stronger base.



17. (i) (a) Cannizzaro reaction : Aldehydes which do not contain an α -H atom undergo disproportionation when heated with concentrated (50 %) NaOH.

HCHO + HCHO
$$\xrightarrow{50 \% \text{ NaOH}}$$

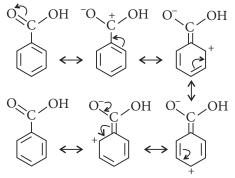
Methanal HCOONa + CH

CHEMISTRY TODAY | DECEMBER '15 63

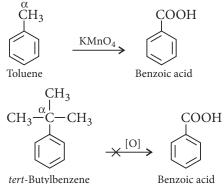
(b) Trans-esterification : An ester on reaction with excess of alcohol in the presence of mineral acid forms a new ester.

$$CH_{3}-C-OCH_{3}+CH_{3}CH_{2}OH \xrightarrow{H^{+}} Methyl ethanoate Ethanol O \\ H \\ CH_{3}OH + CH_{3}-C-OCH_{2}CH_{3} \xleftarrow{} Methanol Ethyl ethanoate$$

(ii) There is high electron density at *meta*-position due to resonance in benzoic acid. Therefore, electrophilic substitution in benzoic acid takes place at *meta*-position.

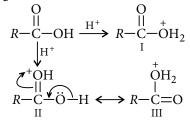


18. (i) Due to absence of benzylic hydrogens, *tert*-butylbenzene does not undergo oxidation to give benzoic acid while other alkylbenzenes such as toluene, ethylbenzene, *n*-propylbenzene and isopropylbenzene which contain one or more benzylic hydrogens undergo oxidation to form benzoic acid.



(No benzylic H, no oxidation)

(ii) Protonation at the hydroxyl oxygen of a carboxylic acid gives structure (I) but protonation at the carbonyl oxygen gives structure (II) which can be regarded as a resonance hybrid of two structures (II and III). Thus, structure (II) is more stable than structure (I) and hence, carbonyl oxygen atom of a carboxylic acid is more basic than hydroxyl oxygen.



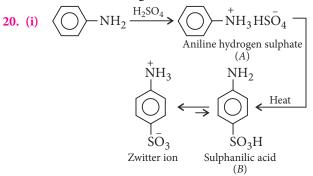
19. (i) The compound 'A' gives a yellow oily substance on treatment with HNO₂. So, it must be a secondary amine. ∴ A is (CH₃)₂NH. (CH₃)₂NH + HONO → (CH₃)₂N−N=O

 $\frac{10}{N-\text{Nitrosodimethylamine}}$ (Yellow oil)

 $+ H_2O$

(ii) 1°, 2° and 3° amines are distinguished by Hinsberg's test. 1° amines react with benzenesulphonyl chloride to give N-alkylbenzenesulphonamide which is soluble in alkali. 2° amines give N,N-dialkylbenzenesulphonamide which is insoluble in alkali and remain unaffected on addition of acid.

3° amines do not react at all and remain insoluble in alkaline solution but dissolves on acidification to give a clear solution.



- (ii) Benzenediazonium chloride is readily soluble in water and is stable in cold water for short time only. It decomposes easily in dry state hence, cannot be stored and is used immediately after preparation.
- (iii) The key step in the Gabriel phthalimide synthesis is a $S_N 2$ reaction in which the nucleophile, phthalimide anion displaces the halide ion from alkyl halide to form *N*-alkylphthalimide. This upon subsequent acid or alkaline hydrolysis gives the corresponding aliphatic primary amine.

Since aryl halides do not undergo nucleophilic substitution reactions easily, therefore, arylamines, *i.e.*, aromatic primary amines cannot be prepared by Gabriel phthalimide reaction.

21. (i)
$$\sum_{C=0+R-Mg-X}^{\delta_{+}} \sum_{Adduct}^{\delta_{+}} \sum_{Adduct}^{R} Mg(OH)X + \sum_{Adduct}^{C} OH \xleftarrow{H_{2}O/H^{+}}_{Hydrolysis}$$
(ii)
$$\sum_{R}^{5} H_{3} - \underbrace{CH}_{-} \underbrace{CH}_{2} - \underbrace{C}_{-} \underbrace{CH}_{3}$$
(iii)
$$\sum_{R}^{5} H_{3} - \underbrace{CH}_{-} \underbrace{CH}_{2} - \underbrace{C}_{-} \underbrace{CH}_{3}$$
(iii)
$$CH_{3} - CH + \underbrace{C+}_{-} CH_{2} - CH - CH_{3} \xrightarrow{[O]}_{-}$$
(iii)
$$CH_{3} - CH + \underbrace{C+}_{-} CH_{2} - CH - CH_{3} \xrightarrow{[O]}_{-}$$
(iii)
$$CH_{3} - CH - CH_{2} - COOH + CH_{3} - CH - COOH$$
3-Methylbutanoic acid 2-Methylpropanoic acid
$$+ \underbrace{O}_{R}_{R}$$
(II)
$$CH_{3} - C - CH_{3}_{R}_{Propan-2-one}$$

Propan-2-one on further oxidation gives a mixture of ethanoic acid and methanoic acid. Subsequent oxidation of methanoic acid gives CO_2 and H_2O .

$$\begin{array}{c} CH_{3}, \\ C=0 \\ CH_{3} \\ CH_{3} \end{array} \xrightarrow{[0]} CH_{3} \\ \hline CH_{3}$$

22. (i) (a) Butanone < Propanol

< Ethanal This is due to increasing +*I* effect of alkyl group from ethanal to butanone

alkyl group from ethanal to butanone which increases the electron density on carbonyl carbon and hence, attack by the nucleophile becomes slower and slower.

(b) Acetophenone < *p*-Tolualdehyde <

Benzaldehyde < *p*-Nitrobenzaldehyde This is due to :

 ketones are less reactive than aldehydes towards nucleophilic addition reactions.

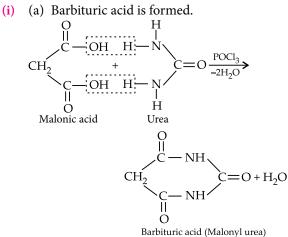
- CH₃ group increases the electron density on carbonyl carbon while nitro group decreases the electron density.
- (ii) $RCOOH + R'OH \xrightarrow{H^+} RCOOR' + H_2O$ Acid Alcohol Ester

The esterification reaction is a reversible reaction. If water and the ester are allowed to remain in the reaction mixture the hydrolysis of the ester would take place. Hence, water or ester should be removed as soon as it is formed.

- **23.** (i) Abhishek showed his concern and responsible nature by emphasizing that one should not play with chemicals in the laboratory.
 - (ii) Acetaldehyde reduces Tollens' reagent to silver mirror but acetone does not. CH₃CHO + 2[Ag(NH₃)₂]⁺ + 3OH⁻ → Acetaldehyde 2Ag↓ + 4NH₃ + CH₃COO⁻ + 2H₂O Silver mirror CH₃COCH₃ Tollens' reagent Acetone No reaction
 - (iii) Clemmensen reduction and Wolff-Kishner reduction.
 - (iv) (a) Acetone is used as a solvent in industries.
 - (b) Acetone is used in the preparation of a number of chemicals such as chloroform ketene, acetic anhydride etc.

CHEMISTRY TODAY | DECEMBER '15

Hence (A) $CH_3 - C - O - CH_2 - CH_2 - CH_2 - CH_3$ (B) CH_3CH_2OH (C) $CH_3CH_2CH_2CH_2OH$ (D) CH_3CHO (E) $CH_3 - CH = CH - CHO$ OR



- (b) Ethanoic acid is formed. $CH_3CHO + O_2 \xrightarrow{\text{cobalt acetate}}{353 \text{ K}} CH_3COOH$
- (ii) (a) Cross aldol condensation : When different aldehydes and ketones containing α -hydrogen atom are treated with dilute alkali, β -hydroxy aldehydes and ketones are formed. This reaction is called cross aldol condensation reaction. If both the reactants contain α -hydrogen atoms then it gives a mixture of four products. *e.g.*,

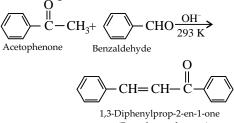
$$CH_{3}CHO + CH_{3}CH_{2}CHO \xrightarrow{1. \text{ NaOH}}{2. \Delta} \xrightarrow{\text{Propanal}} CH_{3}CH = CH - CHO$$

$$But-2-enal$$

$$+ CH_{3}CH_{2}CH = C - CHO + CH_{3}CH = C - CHO$$

$$CH_3 CH_3$$
2-Methylpent-2-enal 2-Methylbut-2-enal + CH_3CH_2CH = CH - CHO
Pent-2-enal

If only one carbonyl compound contains α -hydrogen then only one product is formed. *e.g.*,

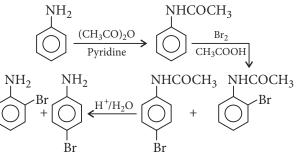


(Benzalacetophenone)

(b) Hell–Volhard–Zelinsky reaction: Carboxylic acids react with chlorine or bromine in the presence of red phosphorous to give compounds in which α -hydrogen atom is replaced by halogen atom.

$$CH_{3}COOH \xrightarrow{Cl_{2}, \text{Red P}} Cl-CH_{2}-COOH \xrightarrow{Cl_{2}, \text{Red P}} Cl_{2}-CHOOH \xrightarrow{Cl_{2}, \text{Red P}} Cl_{2}-CHCOOH \xrightarrow{Cl_{2}, \text{Red P}} Cl_{2}-CHCOOH \xrightarrow{Cl_{2}, \text{Red P}} Oichloroacetic acid \xrightarrow{Cl_{2}, \text{Red P}} Cl_{3}-CCOOH \xrightarrow{Cl_{3}-CCOOH} Trichloroacetic acid$$

25. (i) Monobromoaniline can be prepared by first protecting the amino group by acetylation and then halogenation followed by hydrolysis.



(ii) (a) Coupling reaction : It is the reaction of an aromatic diazonium salt with phenol or aromatic amine at low temperature to give coloured azo compounds.

$$\underbrace{\bigcirc}_{\text{Aniline}}^{+} \text{NH}_{2} \underbrace{\xrightarrow{}_{273 \text{ K}}}_{\text{Aniline}} \text{NH}_{2} \underbrace{\xrightarrow{}_{273 \text{ K}}}_{\text{P-Aminoazobenzene}} \underbrace{\stackrel{p-\text{Aminoazobenzene}}{\text{(Yellow dve)}}$$

- (b) Aqueous ethylamine is basic in nature because of the presence of free OH⁻ ions hence, it turns red litmus blue.
 C₂H₅NH₂ + H₂O → [C₂H₅NH₃]⁺ + OH⁻
- (c) Methylamine being more basic than water, accepts a proton from water liberating OH⁻ ions.

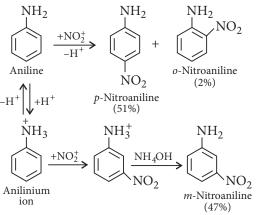
$$CH_3NH_2 + H - OH - CH_3 - H_3 + OH$$

CHEMISTRY TODAY | DECEMBER '15

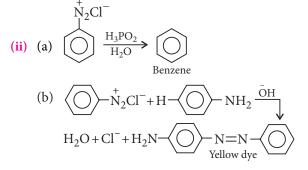
These OH⁻ ions combine with Fe³⁺ ions present in H₂O to form brown ppt. of hydrated ferric oxide. FeCl₃ \longrightarrow Fe³⁺ + 3Cl⁻ 2Fe³⁺ + 6OH⁻ \longrightarrow 2Fe(OH)₃ Hydrated ferric oxide (Brown ppt.)

OR

(i) Nitration is usually carried out with a mixture of conc. HNO₃ + conc. H₂SO₄ (nitrating mixture). In presence of these acids, most of aniline gets protonated to form anilinium ion. Therefore, in presence of acids, the reaction mixture consists of aniline and anilinium ion. Now, -NH₂ group in aniline is *o*, *p*-directing and activating while the -⁺NH₃ group in anilinium ion is *m*-directing and deactivating. Whereas nitration of aniline (due to steric hindrance at *o*-position) mainly gives *p*-nitroaniline, the nitration of anilinium ion gives *m*-nitroaniline. In actual practice, approx. 1 : 1 mixture of *p*-nitroaniline and *m*-nitroaniline is obtained.



Thus, nitration of aniline gives a substantial amount of *m*-nitroaniline due to protonation of the amino group.



(c)
$$\langle \bigcirc + \overset{+}{N_2}Cl^- + H + \bigcirc - OH \xrightarrow{OH} H_2O + Cl^- + HO + \bigcirc N = N + \bigcirc Orange dye$$

- **26. (i)** In weakly acidic medium, the oxygen of the carbonyl group gets protonated which in turn by way of resonance increases the +ve charge on the carbonyl carbon. As a result, a nucleophile like ammonia derivative attacks it readily.
 - (ii) Due to higher electronegativity, electron density shifts towards oxygen and carbon becomes electron deficient and acts as electrophilic centre and oxygen acts as nucleophilic centre.

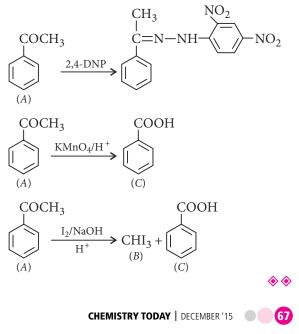
$$c = 0 \longrightarrow -c = 0$$

(iii) 40% aqueous solution of methanal is called formalin and trioxane is a trimer of methanal.



OR

Molecular formula of the compound 'A' is C_8H_8O . As 'A' does not give Tollens' or Fehling's test, it must be a ketone. It gives positive test with 2, 4 - DNP and iodoform test. It means it is a methyl ketone.



EXAMINER'S

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

ALCOHOLS, PHENOLS AND ETHERS | ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- 1. Doctors detect diabetes disease by testing the glucose in urine by
 - (a) Nessler's solution (b) Fehling's solution
 - (c) Fenton's reagent (d) silver nitrate solution.
- 2. Phenol is converted into bakelite by heating it with formaldehyde in the presence of an alkali or an acid. Which statement is true regarding this reaction?
 - (a) The electrophile in both cases is $CH_2 = O$
 - (b) The electrophile in both cases is $CH_2 = OH$
 - (c) The electrophile is $CH_2=O$ in the presence of an alkali and $CH_2 = OH$ in the presence of an acid.
 - (d) It is a nucleophilic substitution reaction.
- 3. The IUPAC name of the following compound is

$$\begin{array}{c} O & O \\ \mathbb{H}_{3} - \mathbb{C} - \mathbb{C} \mathbb{H}_{2} - \mathbb{C} - \mathbb{O} \mathbb{C}_{2} \mathbb{H}_{5} \end{array}$$

- (a) ethyl β -ketobutyrate
- (b) ethyl-3-oxobutanoate
- (c) 1-carbethoxypropanone

4.
$$Y \xleftarrow{CH_3OH}_{CH_3ONa} H_2C \xrightarrow{CHCH_3}_{H^+} X$$

Here 'X' and 'Y' are respectively

(a) $CH_2 - CHCH_3$ and $HOCH_2 - CHCH_3$ OCH₃ OH OCH₃

68

(b)
$$HOCH_2 - CHCH_3$$
 and $CH_2 - CHCH_3$
 $|$ $|$ $|$ $|$
 OCH_3 OCH_3 OH

(c) CH_2 -CHCH₃ in both cases OCH₃ OH

(d)
$$HOCH_2 - CHCH_3$$
 in both cases.
|
OCH_2

5. Which of the following reactions/reagents cannot be used for the given reduction reaction?

$$R > C = O \longrightarrow R > CH_2$$

- (a) Clemmensen reduction
- (b) Wolff-Kishner reduction
- (c) HI/Red P at 200°C
- (d) Wurtz reaction
- 6. The order of reactivity of alcohols towards sodium metal is
 - (a) primary > secondary > tertiary
 - (b) primary < secondary < tertiary
 - (c) primary > secondary < tertiary
 - (d) primary < secondary > tertiary.

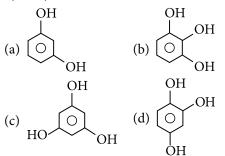
7. In the reaction,
$$(Anisol)$$
 (HI)

the mechanism followed and the major products are respectively

(a)
$$S_N^{1}$$
 \bigcirc and CH_3^{I}
(b) S_N^{2} \bigcirc and CH_3^{OH}

(c)
$$S_N^{2}$$
, \bigcirc and CH_3I
(d) S_N^{1} , \bigcirc and CH_3OH

- 8. An organic compound 'X' on treatment with pyridiniumchlorochromate in dichloromethane gives compound 'Y'. Compound 'Y' reacts with I2 and alkali to form triiodomethane. The compound 'X' is (b) CH₃CHO (a) C_2H_5OH
 - (d) CH₃COOH (c) CH_3COCH_3
- 9. Friedel-Crafts acylation of benzene with benzoyl chloride gives
 - (b) CH₃COCH₃ (a) $C_6H_5COCH_3$
 - (d) none of these. (c) $C_6H_5COC_6H_5$
- 10. Which of the following compounds can react with hydroxylamine?

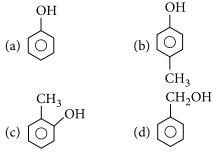


- 11. Ketones react with Mg Hg over water to give
 - (a) pinacolones
 - (b) pinacols
 - (c) benzoquinone
 - (d) benzophenone.
- **12.** Identify the product of the following reaction :

- (a) HOOC(CH₂)₄COOH COOH (b) COOH (c) $CH_3(CH_2)_4CH_3$
- (d) OHC(CH₂)₄CHO
- 13. Dehydration of an alcohol in the presence of sulphuric acid gives alkene. $CH_3CH_2OH \xrightarrow{H_2SO_4} CH_2 = CH_2 + H_2O$

- Here sulphuric acid acts as
- (a) an acid (b) a base
- (d) all of these. (c) a catalyst

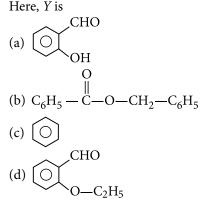
14. Which of the following will decolourise $KMnO_4/H^+$ and change the orange colour of $K_2Cr_2O_7/H^+$ to green?



15. Study the given sequence of reactions :

$$\bigcirc \overset{\text{CH}_3}{\underset{\text{(ii) H_2O/H}^+}{(\text{C}_2H_5O)_3Al}} X \xrightarrow{(C_2H_5O)_3Al} Y$$

(Major product)



16. Major product of the given reaction is

$$\begin{array}{c} CH_{3}CH_{2}-C-CH_{2} & \xrightarrow{NaOH}{H_{2}O^{18}} \\ CH_{3} & H^{18} & OH \\ (a) & CH_{3}CH_{2}-C-CH_{2} \\ & CH_{3} \\ (b) & CH_{3}CH_{2}-C-CH_{2} \\ & CH_{3} \\ (b) & CH_{3}CH_{2}-C-CH_{2} \\ & CH_{3} \\ (c) & CH_{3}CH_{2}-C-CH_{2} \\ & CH_{3} \\ (d) & CH_{3}CH_{2}-C-CH_{2} \\ & CH_{3} \\ (d) & CH_{3}CH_{2}-C-CH_{2} \\ & CH_{3} \\ \end{array}$$

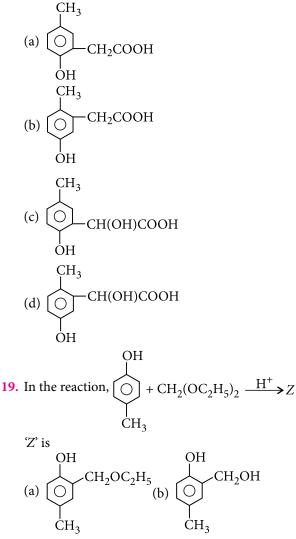
CHEMISTRY TODAY | DECEMBER '15

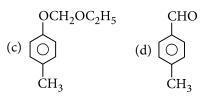
17. Ozonolysis of 2,3-dimethylbut-1-ene gives

(a)
$$CH_3 - C - CH_3 + HCHO$$

(b) $CH_3CH_2CH_2 - C - CH_3 + CH_3CHO$
(c) $H_3C - CH - C - CH_3 + CH_3CHO$
(d) $H_3C - CH - C - CH_3 + HCHO$

18. *p*-Cresol reacts with chloroform in alkaline medium to give a compound '*A*' which adds hydrogen cyanide to form the compound '*B*'. Compound '*B*' on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is





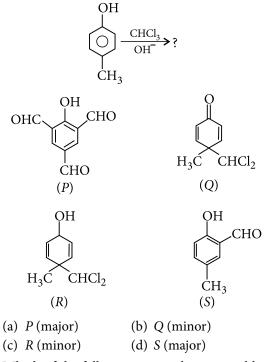
20. Arrange the following compounds in decreasing order of reactivity towards nucleophilic addition reaction.

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. In the following reaction, the product(s) formed is/are



22. Which of the following cannot be prepared by the typical Williamson reaction?

- (a) $R_3 COCR_3$
- (b) ArOAr
- (c) RCH=CHOCH=CHR'
- (d) C₆H₅CH₂OC₂H₅



CHEMISTRY TODAY | DECEMBER '15

- **23.** Which of the following reactions will yield propane?
 - (a) Propanone + H₂ $\xrightarrow{\text{Zn-Hg}}_{\text{HCl}}$

(b) Propyne +
$$2H_2 \xrightarrow{Ni}$$

(c) Propanone + H₂
$$\frac{(i) \text{ NH}_2 \text{NH}_2}{(ii) \text{ KOH/Ethylene glycol}}$$

- (d) Propanone $\xrightarrow{\text{NaBH}_4}$
- **24.** Which of the following compounds can be used as an acylating agent?
 - (a) CH_3COCl (b) $(CH_3CO)_2O$
 - (c) CH_3COOH (d) CH_3CH_2COCl
- **25.** Which of the following compounds will undergo reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid?
 - (a) Butanol (b) Benzaldehyde
 - (c) Phenol (d) Benzoic acid

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Alcohols and phenols consist of two parts, an alkyl/aryl group and a hydroxyl group. The properties of alcohols and phenols are chiefly due to the hydroxyl group. The nature of alkyl and aryl groups simply modify these properties.

- **26.** Which of the following is most reactive towards aqueous HBr?
 - (a) 1-Phenyl-1-propanol
 - (b) 1-Phenyl-2-propanol
 - (c) 3-Phenyl-1-propanol
 - (d) None of these
- 27. The order of solubility of the given compounds in water is

$$H_{3}C \xrightarrow{O} CH_{3} H_{3}C \xrightarrow{O} H H_{5}C_{2} \xrightarrow{O} H$$

$$I \qquad II \qquad III$$
(a) I > II > III (b) I < II < III
(c) II > III > I (d) II < I < III

28. What is the order of reactivity of different types of alcohols in the reaction given below?

$$R - OH + HX \longrightarrow RX + H_2O$$

- (a) tertiary > secondary > primary
- (b) tertiary < secondary < primary
- (c) tertiary > primary > secondary
- (d) secondary > primary > tertiary

Paragraph for Questions 29 to 31

The aldehydes and ketones undergo nucleophilic addition reactions. A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from sp^2 to sp^3 in this process and a tetrahedral alkoxide intermediate is produced.

29. The increasing order of the rate of HCN addition to the given compounds is

I. HCHO	II. CH ₃ COCH ₃
III. PhCOCH ₃	IV. PhCOPh
(a) $I < II < III < IV$	(b) $IV < II < III < I$
(c) $IV < III < II < I$	(d) $III < IV < II < I$

30. Which of the following is an example of nucleophilic addition?

(a)
$$C_6H_5 - \overset{O}{C} - CH_3 \xrightarrow{NH_2NH_2,H^+} C_6H_5 - \overset{H}{C} - CH_3$$

 $O \qquad OH$
(b) $C_6H_5 - \overset{H}{C} - CH_3 \xrightarrow{LiAlH_4} C_6H_5 - \overset{I}{C} - CH_3$

- (c) Both (a) and (b)
- (d) None of these
- **31.** Which carbonyl group of the given compound is most reactive for nucleophilic addition reaction?



- (a) 1
- (b) 2
- (c) 3
- (d) All have equal reactivity.

CHEMISTRY TODAY | DECEMBER '15

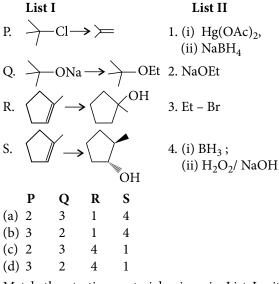


SECTION - IV

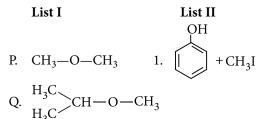
Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

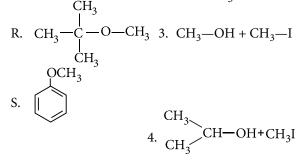
32. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the codes given below the lists:



33. Match the starting materials given in List I with the products formed by these with HI given in List II and select the correct answer using the codes given below the lists :



2. $CH_3 - CH_3$ $CH_3 - C - I + CH_3OH$ CH_3



	Р	Q	R	S
(a)	1	2	3	4
(b)	4	3	2	1
(c)	3	4	2	1
(d)	3	4	1	2

34. Match the reactions given in List I with the suitable reagents given in List II and select the correct answer using the codes given below the lists :

		U		U			
		L	ist I			Li	st II
P.	Benzophenone \rightarrow Diphenylmethane			1.	LiAlH ₄		
Q. Benzaldehyde \rightarrow 1-Phenylethanol				2.	DIBAL—H		
R.	Cycl	ohexa		\rightarrow yclohe	xanol	3.	Zn-Hg/ Conc. HCl
S.	Phe	nyl ber		$e \rightarrow$	ehyde	4.	CH ₃ MgBr
	Р	Q	R	S			
(a)	3	-	1	2			
(b)	4	3	1	2			
(c)	1	2	4	3			
(d)	1	3	2	4			
			SEC	TION	- V		
				-	_		

Assertion Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- **35. Assertion :** Reimer–Tiemann reaction of phenol with CCl₄ in NaOH at 340 K gives salicylic acid as the major product.
 Reason : The reaction occurs through intermediate

formation of dichlorocarbene.

- **36.** Assertion : With HI at 373 K, methyl *tert*-butyl ether gives *tert*-butyl iodide and methanol. **Reason :** The reaction occurs by $S_N 2$ mechanism.
- **37.** Assertion : Claisen condensation of CH_3 — $COOC_2H_5$ (on heating with C_2H_5ONa) produces ethyl acetoacetate.
 - **Reason :** Ethyl acetoacetate gives the tests of -C and $-COOC_2H_5$ functional groups only.

38. Assertion : Acetaldehyde on treatment with alkali gives aldol.

Reason : Acetaldehyde molecule contains α -hydrogen atom.

39. Assertion : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

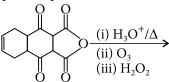
40. Assertion : p*K*_{*a*} value of phenol is lower than that of ethanoic acid.

Reason : Phenoxide ion is more resonance stabilised than *R*COO⁻ ion.

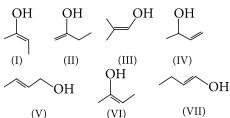
SECTION - VI Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. In the given reaction, the total number of carboxylic groups in the product is



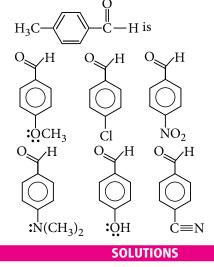
- **42.** When ethanal reacts with propanal in the presence of a base, the number of products formed is
- **43.** When Glucose, [OHC(CHOH)₄CH₂OH] is oxidised with periodic acid, number of moles of formic acid obtained by one mole of glucose is
- **44.** In the given list of compounds, number of compounds which are enol forms of 2-butanone is



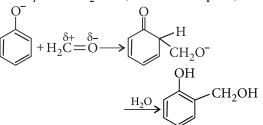
- **45.** Acetylation of a polyhydric alcohol increases its molecular mass by 126 units. The number of 'OH' groups in the molecule is
- **46.** Number of isomers of C₅H₁₁OH which are primary alcohols is
- **47.** Number of products formed by 1, 2-diethylbenzene on ozonolysis is
- **48.** Number of alcohols which are chiral in nature with molecular formula $C_4H_{10}O$ are

49. Number of moles of 'HI' which will react with OCH₃

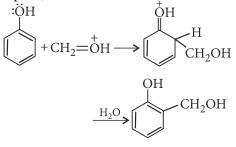
50. From the following compounds, the number of compounds which show(s) higher rate of nucleophilic addition than



- 1. (b): Simple sugars *e.g.*, glucose give a positive test with Fehling's solution thus it is used to test the presence of glucose in urine for detecting diabetes.
- 2. (c) : Condensation of phenol with formaldehyde is an electrophilic substitution reaction. Base converts phenol into phenoxide ion which being more reactive, reacts easily with $CH_2 = O$ (a weak electrophile).



In presence of an acid, $CH_2 = O$ (a weak electrophile) is protonated to $CH_2 = OH$ (a strong electrophile) which easily reacts with phenol (a weak nucleophile).



CHEMISTRY TODAY | DECEMBER '15

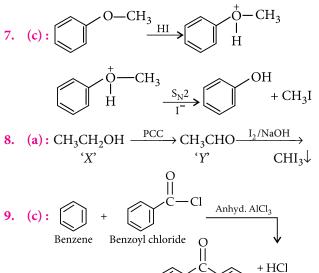
- 3. (b)
- 4. (b): In the acid-catalysed ring opening of an unsymmetrical epoxide, the nucleophile attacks primarily at the more substituted carbon atom because such atom of the protonated epoxide acquires a considerable positive charge. This resembles a more stable 2° or 3° carbocation and hence, the reaction is $S_{\rm N}1$ like.

$$\begin{array}{c} H_{2}C - CHCH_{3} \xrightarrow{CH_{3}OH} H_{2}C - CHCH_{3} \\ \downarrow \\ O \leftarrow \\ H \\ H \\ H \\ - H^{+} H_{2}C - CHCH_{3} \\ \downarrow \\ H \\ - H^{+} H_{2}C - CHCH_{3} \\ \downarrow \\ OH \\ OCH_{3} \end{array}$$

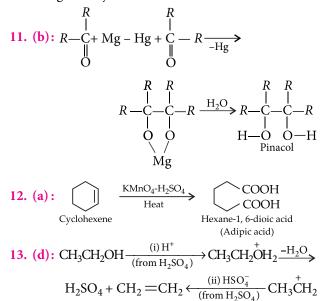
In case of CH_3ONa , $-OCH_3$ being a strong nucleophile, opens the strained epoxide ring in a direct S_N^2 reaction, *i.e.*, by attacking at the least hindered carbon atom.

$$\begin{array}{c} H_2C - CHCH_3 \longrightarrow CH_3OCH_2CHCH_3 \\ O & OH \end{array}$$

- 5. (d): Wurtz reaction cannot be used for this reduction.
- 6. (a) : Due to +*I* effect of alkyl groups, the O—H bond in tertiary alcohols is the strongest and hence most difficult to break followed by the O—H bond in secondary alcohols while the O—H bond in primary alcohols is the weakest. Lower the degree of alcohol, higher is the acidic character and easier is the displacement of hydrogen of —OH group by Na.



10. (c) : We know that phenols show keto-enol tautomerism and the stability of the keto form depends upon the number of keto groups. More the number of keto groups, higher will be stability of the keto tautomer. Thus trihydric phenols should exist in keto form in considerable amount but only when the two keto groups are not on adjacent carbon atoms which decreases stability due to positive charge on adjacent carbon atoms.



 $\rm H_2SO_4$ is acting as an acid in step (i) and a base in step (ii). Since it is regenerated back as such, it also acts as a catalyst.

CH₂OH ↓

14. (d): O is an alcohol which is oxidised by

 $KMnO_4/H^+$ and $K_2Cr_2O_7/H^+$.

Pink-purple colour of $KMnO_4/H^+$ vanishes due to the formation of $MnSO_4$ while orange colour of $K_2Cr_2O_7/H^+$ changes to green due to the formation of $Cr_2(SO_4)_3$.

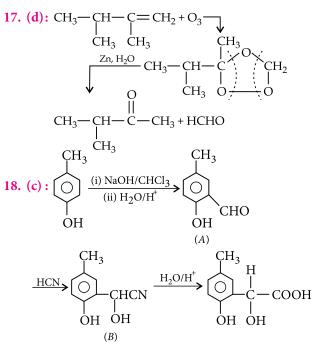
15. (b): 'X' is
$$\bigcirc$$
 CHO formed by Etard reaction
and 'Y' is $C_6H_5-C-O-CH_2-C_6H_5$ formed by Tischenko reaction.

16. (b): Base catalysed epoxide opening is a typical S_N^2 reaction in which attack of the nucleophile takes place at the less hindered expoxide.

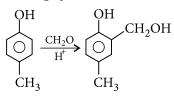


CHEMISTRY TODAY | DECEMBER '15

Benzophenone



19. (b): $CH_2(OC_2H_5)_2$ is an acetal of formaldehyde with ethanol. In presence of an acid, it decomposes to CH₂O and C₂H₅OH.



20. (d): Ketones are less reactive than aldehydes due to the presence of two large electron releasing alkyl groups, which hinder the attack of nucleophile on the carbonyl carbon and also reduces the electrophilicity of the carbonyl carbon.

As the size of the alkyl group increases, +I effect increases and thus reactivity decreases. Aromatic aldehydes and ketones are less reactive due to +R effect of the benzene ring.

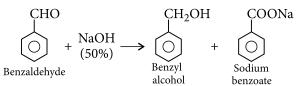
Thus, the decreasing order of reactivity towards nucleophilic addition reaction is :

$$\label{eq:ch3} \begin{array}{c} CH_{3}CHO > CH_{3}CH_{2}CHO > C_{2}H_{5}COC_{2}H_{5} > \\ IV \qquad III \qquad I \\ C_{6}H_{5}CHO \\ II \end{array}$$

21. (b, d) : It is Reimer-Tiemann reaction.

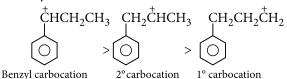
22. (a, b, c) : tert- and sec-carbocations are liable to undergo elimination reaction in presence of strong alkoxide bases. Aryl and vinyl halides do not undergo nucleophilic substitution.

- **23.** (a, b, c) : (a) is Clemmensen reduction. (b) is catalytic reduction. (c) is Wolff—Kishner reduction. (d) Ketones with sodium borohydride give secondary alcohols.
- 24. (a, b, d) : Stronger the basic nature of the leaving group, weaker will be its leaving ability. In CH₃COOH, OH⁻ is a strong base so it cannot be removed easily to form CH_3CO required for acylation.
- 25. (b): It is Cannizzaro reaction.



26. (a): Carbocation is formed as an intermediate hence, the species capable of forming most stable carbocation will be most reactive.

Stability of carbocation follows the order :



27. (c)

28. (a): Reaction of alcohols involving cleavage of C—OH bond follows the reactivity order : Tertiary > secondary > primary, according to the

stability of carbocation intermediate.

29. (c): Addition of HCN to carbonyl compounds is a characteristic nucleophilic addition reaction of carbonyl compounds.

Order of reactivity :

$$H C = O > R C = O > R C = O$$

The lower reactivity of ketones over aldehydes is due to +I effect of the alkyl (R) group and steric hindrance. As the size of the alkyl group increases, the reactivity of the ketones further decreases.

The aromatic aldehydes and ketones are less reactive than their aliphatic analogues. This is due to the +R effect of the benzene ring.

Hence, the increasing order of the rate of HCN addition to compounds HCHO, CH₃COCH₃, PhCOCH₃ and PhCOPh is

PhCOPh < PhCOCH₃ < CH₃COCH₃ < HCHO.

CHEMISTRY TODAY | DECEMBER '15 75

(b) In the reduction of carbonyl group with LiAlH₄ or NaBH₄, a hydride ion is transferred from the metal to the carbonyl carbon (nucleophilic addition).

$$C = O + H \rightarrow AlH_3 \longrightarrow -C - OAlH_3$$

31. (b) 32. (a)

P : 3° Chloro compound is converted to ethene by EtONa.

Q : It is Williamson synthesis giving ether by EtBr.

R : It is Markovnikov's addition by oxymercuration demercuration.

S : It is hydroboration oxidation which lead to anti-Markovnikov's addition.

33. (c)

34. (a)

- **35.** (c) : Nucleophilic attack of phenolate ion through the *ortho*-carbon atom occurs on CCl_4 (a neutral electrophile) to form an intermediate which on hydrolysis gives salicylic acid.
- **36.** (c) : The reaction occurs by $S_N 1$ mechanism :

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{C} OCH_{3} + HI \xrightarrow{373 \text{ K}} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{C} OCH_{3} + HI \xrightarrow{373 \text{ K}} \xrightarrow{C} OCH_{3} \xrightarrow{C}$$

 $CH_{3} - C - OC_{2}H_{5} + H - CH_{2} - COOC_{2}H_{5} + C_{2}H_{5}ONa$ O $CH_{3} - C - CH_{2}COOC_{2}H_{5} + C_{2}H_{5}OH$ Ethyl acetoacetate

It exists as :

$$CH_{3}-C-CH_{2}-COOC_{2}H_{5} \longleftrightarrow$$

$$CH_{3}-C-CH_{2}-COOC_{2}H_{5} \longleftrightarrow$$

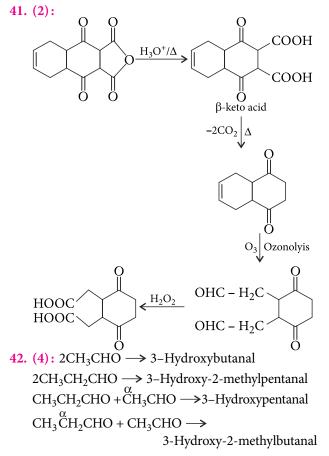
$$CH_{3}-C-CH_{2}-COC_{2}H_{5}$$

$$CH_{3}-C-CH_{2}-COC_{2}H_{5}$$

$$C=C, -C- \text{ and } -COOC_{2}H_{5}.$$

$$CH_{3}-CH_{2}-CH_{2}-CHO \xrightarrow{OH}_{Aldol} OH_{2}-CH_{2}-CHO$$

- **39.** (c) : Aromatic aldehydes and formaldehyde do not contain α -hydrogen atom and thus, undergo cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.
- **40.** (d): Phenol is less acidic than acetic acid and has higher pK_a value than that of CH₃COOH.





4

43. (5)
$$C_6H_{12}O_6 \xrightarrow{\text{HIO}_4} \text{5HCOOH} + \text{HCHO}_{\text{Formic acid}} + \text{HCHO}_{\text{Formaldehyde}}$$

- **44.** (3): I, II and VI are enol tautomers of 2-butanone.
- **45. (3):** Acetylation of alcohol increases the mass by 42 units per —OH group.

No. of -OH groups =
$$\frac{\text{Increase in mass}}{42} = \frac{126}{42} = 3$$

5. (4): (i) CH₃CH₂CH₂CH₂CH₂OH
(ii) CH₃CH₂-CH-CH₂OH
CH₃
(iii) CH₃-CH-CH₂-CH₂OH
CH₃
CH₃

(iv)
$$CH_3 - CH_2OH$$

 CH_3

order :

47. (3): 1, 2– Diethylbenzene is a resonance hybrid of the two structures which on ozonolysis give three different products.

(i) (a) The typical reactions of benzene are

electrophilic substitution reactions. Higher the electron density in the benzene ring,

more reactive is the compound towards

these reactions. Since, $-NO_2$ is a more

powerful electron withdrawing group than

-Cl, therefore, more the number of nitro

groups, less reactive is the compound. Thus, the overall reactivity decreases in the

Chlorobenzene > *p*-nitrochlorobenzene

(b) Here, -CH₃ group is electron donating

but $-NO_2$ group is electron withdrawing.

Therefore, the maximum electron-density

will be in toluene, followed by p-nitrotoluene

followed by *p*-dinitrobenzene. Thus, the overall reactivity decreases in the order :

Toluene > *p*-nitrotoluene > *p*-dinitrobenzene

the intermediate. Therefore, anhy. AlCl₃ first

reacts with *n*-propyl chloride to form *n*-propyl

cation. This being 1° is less stable and hence,

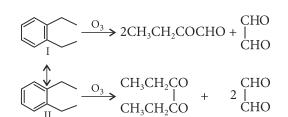
rearranges to the more stable 2° carbocation,

(ii) During Freidel-Crafts reaction, carbocation is

> 2, 4-dinitrochlorobenzene

Contd. from page no.23

YOUR WAY CBSE XI

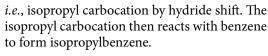


48. (1): Only one alcohol contains chiral carbon atom.

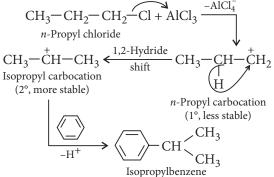
Only III is chiral in nature.

49. (6)

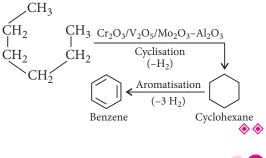
۵ ۵



50. (3)



(iii) When vapours of hexane are passed over heated catalyst consisting of Cr_2O_3 , Mo_2O_3 , and V_2O_5 supported over Al_2O_3 at 773 K under 10-20 atm pressure, cyclisation and aromatisation occur simultaneously to give benzene.



CHEMISTRY TODAY | DECEMBER '15



Mukul C. Ray, Odisha

Oxidation States of 3*d***-Series Elements**

On moving across the 3d-series, the nuclear charge increases at each stage with addition of one proton to the nucleus. Also, inner core electrons increase as electrons enter into 3*d*-subshell. The outermost shell for these elements are the 4s-electron(s). The 3d-electrons do not screen the nuclear charge more effectively as the 3d-orbitals are diffused in shape. As a consequence, the effective nuclear charge increases and 3d-electrons experience more and more nuclear charge. They become progressively more stabilised across the series. In other words, as the nuclear charge increases, the energy of 3d-electrons falls well below that of 4s electrons and the elements in the later half of the series typically exhibit oxidation state of II, which corresponds to removal of only two 4s-electrons. Higher oxidation states of these elements are produced with difficulty. Following are the distinguished points :

- Ti(II), V(II) and Cr(II) are good reducing agents as they have tendency to lose 3*d*-electrons. On moving towards right in the series, the 3*d*-electrons become more stable and are reluctant to be lost.
- Mn(VII), Cr(VI), V(V) oxidation states exist as permanganate, dichromate or chromate and vanadate respectively. These high oxidation states are the results of loss of 3*d*-electrons. Since 3*d*-electrons become increasingly stable, these ions have a tendency to fill their *d*-orbitals and hence they act as oxidising agents. The oxidising ability increases as expected in the order :

V(V) < Cr(VI) < Mn(VII).

- These elements form compounds in lower oxidation states of (I), (0) and even negative with pi acid ligands (a part of coordination complexes). Cu(I) compounds are relatively stable due to $3d^{10}$ configuration.
- Mainly ionic compounds are formed by all elements except Sc in the oxidation state II. The oxides are

basic and the halides are ionic. With increase in the atomic number, the divalent state becomes more stable.

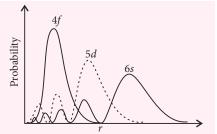
- Oxidation state III is exhibited by all the elements except Zn. Sc(III) is very stable whereas Cu(III) is highly oxidising.
- Oxidation state IV is important only for Ti and V, while for the rest of the elements, it is found only in oxo and fluoro complexes.

Oxidation States of *d***-Block Elements**

As the atomic number increases, the energy of all orbitals tends to fall. The difference in penetrating power now plays the key role. The *s*-obital is compact but *d*-orbital is diffused. Both feel contracted but *d*-orbital experiences more contraction. As a result, when we move down the group, the energy gap between *ns*- and (n - 1)d-orbitals decreases. Now, both these kind of electrons are available towards bonding under similar circumstances. So higher oxidation states now become more probable. Iron fails to show VIII oxidation state, whereas osmium in the same group shows VIII oxidation state in OsO₄.

Oxidation States of Inner Transition Elements

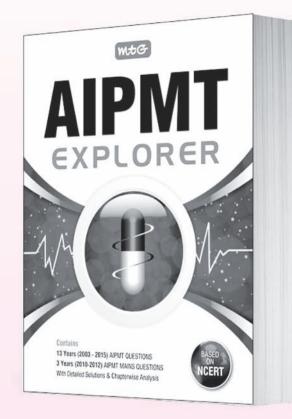
The lanthanides are those elements in which the 4f-orbitals are gradually filled. At lanthanum, the 5d-orbital is lower in energy than 4f-orbital. As more protons are added to the nucleus, the 4f-orbitals contract rapidly and become more stable than the 5d-orbitals and electrons start entering the 4f-orbital.



The penetration of different orbitals is shown. The 6*s*-orbital penetrates to the inner core.



Last-minute check on your AIPMT readiness



₹500

MTG's AIPMT Explorer helps students self-assess their readiness for success in AIPMT. Attempting the tests put together by MTG's experienced team of editors and experts strictly on the AIPMT pattern and matching difficulty levels, students can easily measure their preparedness for success. Order now!

HIGHLIGHTS:

- · 10 Model Test Papers based on latest AIPMT syllabus
- · Last 13 years' solved test papers of AIPMT
- Includes solved AIPMT 2015 paper
- Detailed solutions for self-assessment and to practice time management

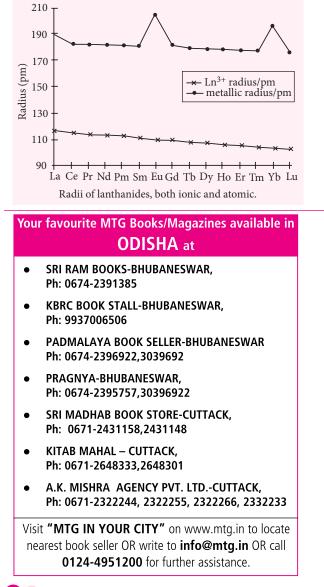


Available at all leading book shops throughout the country. For more information or for help in placing your order: Call 0124-4951200 or email: info@mtg.in *Application to read QR codes required



Scan now with your smartphone or tablet*

Visit www.mtg.in for latest offers and to buy online! Along the series, there is a decrease in both the atomic and ionic radii of the Ln³⁺ ions. The 4*f*-electrons are inside the 5s- and 5p-electrons and are core-like in their behaviour being shielded from the bonded groups. The 5s- and 5p-orbitals and also the 6s-orbitals penetrate the 4f-subshell and are not shielded from increasing nuclear charge and hence, because of the increasing effective nuclear charge, they contract as the atomic number increases. Lanthanide contraction is sometimes spoken as if it were unique. But similar phenomena also exists like actinide contraction, scandide contraction. The abrupt increase in atomic size for europium and ytterbium is because they donate only two electrons (associated with stability of half filled and fully filled orbitals) whereas others donate three electrons to the electron pool of metallic crystal.



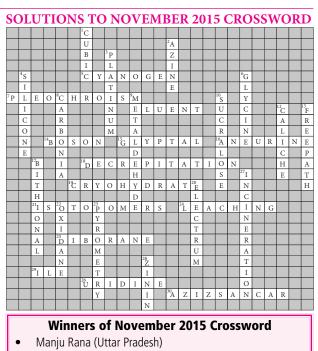
Now, it can be concluded that III is the most common oxidation state of lanthanides both in solid state and in aqueous solutions. Lattice energy in solid state and hydration energy in aqueous solution are so adjusted that they support III oxidation state for lanthanides. The notables points are :

- The III oxidation state is generally the more stable for Ln.
- Other oxidation states are available, especially if a $4f^0$, $4f^7$ and $4f^{14}$ configuration results.
- The most accessible 2+ ions are $Eu^{2+}(4f^7)$ and $Yb^{2+}(4f^{14})$.
- The most accessible 4+ ions are $Ce^{4+}(4f^0)$ and $Tb^{4+}(4f^{14})$.

In actinides, the energy gap between 5f-orbital and 7s-orbital decreases. The 5f-electrons are now easily available for bonding. They are not deeply seated as 4f-electrons. Hence, actinides show higher oxidation states. Uranium, for example shows VI oxidation state. The highest oxidation state shown by any actinide is VII.

As the 4*f*-electrons are deeply held, the magnetic properties of lanthanides are largely independent of environment. In case of actinides, the magnetic properties are highly complex.

، ا



• Ritesh Rao (Karnataka)

CHEMISTRY TODAY | DECEMBER '15



Bhutan to pave `green' roads with plastic

Bhutan has come up with a new way to pave its roads : waste plastic. As part of efforts to curb the use of fossil fuels and deal with growing amounts of plastic waste, the country plans to mix used plastic bottles and other waste plastic with bitumen to blacktop its roads.

The Green Road public private project is expected to reduce the amount of bitumen imported from India by 40% and cut the amount of plastic waste going into landfills by 30-40% said plastic road entrepreneur Rikesh Gurung.

Although only 10 to 15% of the mix used to pave roads is plastic, the project is expected to consume all the plastic waste in the country of over 7,80,000 people, Gurung said.

"We will use the plastic waste to build eco-friendly and durable roads..." said the 30-year-old, who in October built an initial 150-metre length of pilot road in the capital, Thimphu.

"Recycling plastic waste and not burning (it) is the correct approach to protect the environment," he said. Gurung came across the idea of using plastic waste in blacktopping roads when he was studying at Thiagarajar College of Engineering in India's Madurai.

Acid fog dissolved rocks on Mars

FROM

VASTE PLASTIC

Mars has acid fog which eats away rocks and is caused by volcanic eruptions on the red planet, a new study suggests.

A planetary scientist has found how acidic vapours may have eaten at the rocks in a 100-acre area on Husband Hill in the Columbia Hills of Gusev Crater on Mars. Shoshanna Cole's research focused on the `Watchtower Class' outcrops on Cumberland Ridge and the Husband Hill summit. "The special thing about Watchtower Class is that it's very widespread which means that the rocks record environments that existed on Mars billions of years ago," she said.

By combining data from previous studies of the area on Mars, Cole saw some intriguing patterns emerge. Spirit examined Watchtower Class rocks and the chemical composition of these rocks, as determined by Spirit's Alpha Proton X-ray Spectrometer, is the same, but the rocks looked different to all of the other instruments.





New insulin pill may replace jabs

Indian-origin scientists are developing a patch for diabetics that attaches to the intestinal wall and releases insulin after being swallowed in the form of a pill. Existing marketed insulin formulations are injectables -currently, it is not possible for insulin to be taken by mouth. Samir Mitragotri, a professor in the college of engineering at the University of California Santa Barbara, and Amrita Banerjee, a postdoctoral fellow, developed patches made of mucoadhesive polymers loaded with insulin and an intestinal permeation enhancer, then placed the patch devices in enteric-coated capsules.

CHEMISTRY MUSING

SOLUTION SET 28

1. (d):
$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

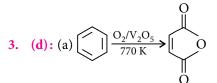
 $3I_2 + 6Na_2S_2O_3 \longrightarrow 3Na_2S_4O_6 + 6NaI$

1 mol K₂Cr₂O₇ $\xrightarrow{\text{KI}}$ 3 mol I₂ \equiv 6 mol Na₂S₂O₃

2. (d): (a) Extensive properties depend on the mass of substance.

(b) If expressed in terms of per mole, the mass of substance is fixed so for one mole of substance it remains same.

(c) Extensive property depends upon two variables and number of moles in case of solution of two substances.



(b) HI formed as a byproduct, is very strong reducing agent which can convert $C_6H_5 - I$ back to benzene. Thus, strong oxidising agent is used.

(c)
$$3CH_3 - C - CH_3 \xrightarrow{\text{conc. } H_2SO_4} CH_3 \xrightarrow{CH_3} CH_3$$

Mesitvlene

(d) π -electrons are delocalised in benzene hence, it does not decolourise bromine water.

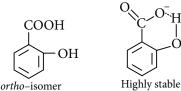
5. (c) : (a)
$$OH$$
 (-*I* pronounced at *meta*-position and not +*R*, acidic strength increases) OH

(b) -R groups increase the acidic strength so, *ortho* and *para*-nitrobenzoic acids are more acidic. Also, *ortho*-nitrobenzoic acid is more acidic than *para*-isomer due to ortho effect. In *meta*-isomer only, -I effect is operative, so it is less acidic than *ortho* and *para*-isomers.

(c) Lesser the charge density, more stable is the base. The stability of conjugate base is $F^- > OH^- > CH \equiv C^- > NH_2^-$ Hence, the order of acidic strength is

 $HF > H_2O > CH \equiv CH > NH_3$

(d) Hydroxybenzoic acids: -OH group is a +R group so acidic strength of benzoic acid should decrease but in *ortho*-isomer, the conjugate base is highly stable due to intramolecular H-bonding.

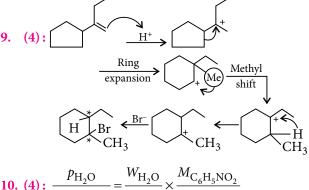


In *meta*-isomer, -I effect increases acidic strength whereas in *para*-isomer, +R effect dominates and its acidic strength is less than that of the benzoic acid.

7. (c):
$$Z = \frac{PV}{RT}$$

If values of critical constants are used, $Z = \frac{P_c V_c}{RT_c} = \frac{3}{8}$

8. (c) : *Z* < 1 *i.e.*, *PV* < *nRT* and attractive forces are dominating. Therefore, gram molar volume will be less than 22.4 L at STP.



$$p_{C_6H_5NO_2} = M_{H_2O} \times W_{C_6H_5NO_2}$$

$$p_{H_2O} = 733 \text{ mm Hg}, p_{C_6H_5NO_2} = 27 \text{ mm Hg},$$

$$M_{H_2O} = 18 \text{ g mol}^{-1}, M_{C_6H_5NO_2} = 123 \text{ g mol}^{-1}$$

$$\frac{W_{H_2O}}{W_{C_6H_5NO_2}} = \frac{733}{27} \times \frac{18}{123} = 3.972 \approx 4$$

Solution Senders of Chemistry Musing SET 28

- 1. Manmohan Krishna (Patna)
- 2. Debdutta Bose (West Bengal)
- 3. Shreya Sharma (Ambala)





Do you have a question that you just can't get answered?

Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

The best questions and their solutions will be printed in this column each month.

Q1. Is it possible for a strong acid like HNO_3 to act as a proton acceptor? If yes, please mention the conditions.

(Udit Mahajan, Chandigarh)

Ans. The capacity of an acid to donate protons depends upon the base strength of the solvent which acts as the proton acceptor. For example, in acetic acid the ionisation of a strong acid H*A* can be represented as :

 $HA + CH_{3}COOH \xrightarrow{\longrightarrow} CH_{3}COOH_{2}^{+} + A^{-}$ Acid Base Acid Base (solvent)

The equilibrium cannot lie much to right since acetic acid has small tendency to accept proton. Therefore, even the strong acids ionise feebly in acetic acid.

However, in hydrogen fluoride, which has no proton accepting tendency at all even the strongest acid is incapable of acting as a proton donor. Thus, nitric acid will ionise slightly as a base in hydrogen fluoride solution.

 $\frac{\text{HNO}_3 + \text{HF}}{\text{Base}} \xrightarrow{\text{Acid}} \frac{\text{H}_2\text{NO}_3^+ + \text{F}^-}{\text{Acid}} \xrightarrow{\text{Base}} \frac{\text{Acid}}{\text{(solvent)}}$

Q2. I have seen in laboratory, that pure lead and pure zinc do not dissolve in acid solutions easily but do so if air is bubbled through the solution. Please explain the reason.

(Sanket Aggarwal, Delhi)

Ans. The standard electrode potential (E°) of lead is -0.13 volt. It should, therefore, dissolve readily in dilute hydrochloric acid, evolving hydrogen. Zinc ($E^{\circ} = -0.76$ volt) should do so even much more readily. However, in actual practice, neither lead



nor pure zinc dissolves in hydrochloric acid and no evolution of hydrogen occurs. This is because of hydrogen overvoltage. The bubble overvoltage of hydrogen over lead is 0.64 volt and that over zinc is 0.70 volt.

In the presence of an oxidising agent like oxygen (air), pure lead or zinc gets oxidised but there may be no evolution of hydrogen gas as it may get oxidised as soon as formed. Similarly, zinc (or any other base metal like lead, iron, etc.) will dissolve easily when it contains other metal having low hydrogen overvoltage as an impurity. In such a case, zinc dissolves producing Zn^{2+} ions while hydrogen is liberated on the impurity part of the zinc rod itself.

Q3. Recently read in newspaper that processed or red meat can cause cancer. Explain.

(Aradhita Roy, West Bengal)

Ans. *N*-Nitrosamines are very powerful carcinogens which scientists fear may be present in many foods, especially in cooked meats that have been cured with sodium nitrite.

Sodium nitrite is added to many meats (*e.g.*, bacon, ham, frankfurters, sausages, and corned beef) to inhibit the growth of *Clostridium botulinum* (the bacterium that produces *botulinum toxin*) and to prevent red meats from turning brown. (Food poisoning by *botulinum toxin* is often fatal.) In the presence of acid or under the influence of heat, sodium nitrite reacts with amines which are always present in the meat to produce *N*-nitrosamines. Cooked bacon, for example, has been shown to contain *N*-nitrosodimethylamine and *N*-nitrosopyrrolidine.

However, nitrites (and nitrates that can be converted to nitrites by bacteria) which occur naturally in many foods may produce nitrosamines when they react with amines in the presence of the acid found in the stomach but, researchers revealed that due to protective effects of nutrients such as vitamin C in vegetables inhibit the formation of toxic nitrosamines. Thus, manufacturers of processed meat are instructed to add antioxidant vitamin C or vitamin E while processing of meat. Also, FDA reduced the permissible amount of nitrites allowed in cured meats from 200 parts per million (ppm) to 50–125 ppm.



iranchembook ir/edu



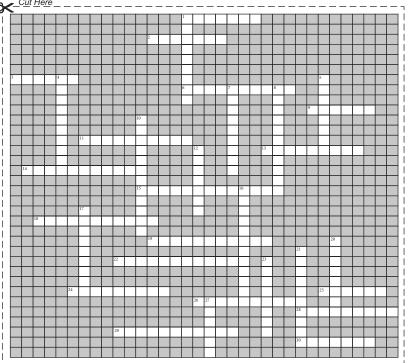
Readers can send their responses at editor@mtg.in or post us with complete address by 25th of every month to win exciting prizes. Winners' name with their valuable feedback will be published in next issue.

ACROSS

- 1. Measure of lifting capacity of hot air. (7)
- 2. Substance formed when acetylene combines with ammonia at high temperature. (7)

GROSS

- 3. Purest variety of silica. (6)
- 6. Reagents having electron attracting and electron repelling sites. (10)
- **9.** Metal present in vitamin B_{12} . (6)
- 11. Bursting of RBCs when placed in pure water. (10)
- An organometallic species that reacts like a carbene. (9)
- **14.** Glassy mass formed on first heating sucrose slowly and then cooling it. (11)
- 15. Another name for oxoprocess. (13)
- A highly branched polymer of α-D-glucose units. (11)
- **19.** Elements which combine primarily with oxygen and are most abundant in earth crust. (11)
- 22. Nuclei having only one stable isotope. (12)
- **24.** The term catalysis was coined by _____. (9)
- **25.** Series of spectral lines of hydrogen atom which lie in the visible region. (6)
- 26. A hypnotic drug. (10)
- **28.** An indicator used for the titration involving weak acid and weak base. (9)
- 29. A sulphide ore of iron and nickel. (11)
- **30.** A smokeless explosive obtained by mixing glyceryl trinitrate with gun cotton and vaseline. (7)
- DOWN
- 1. Geometry of F_2 SeO. (9)
- **4.** Crystal system having five planes of symmetry and five axes of symmetry. (10)
- 5. Product of dehydration of glycerol with KHSO₄. (8)
- 7. Binary compounds of group 15 elements. (9)



- 8. Name of $H_9O_4^+$ ion. (11)
- An acid which exists as a white solid containing octahedral Te(OH)₆ molecules. (12)

MORD

- **12.** Another name of isotope ²¹⁹Rn. (7)
- 16. Reactions having molecularity equal to three. (12)
- A polymer which forms water resistant and quick drying fibre. (9)
- A synthetic organic compound used as anaesthetic in dentistry. (8)
- Carbonyl compounds containing metal and CO only. (10)
- **23.** The process in which particles of dispersed phase unites to form thread like chains which become semisolid and particles of dispersion medium get trapped in the cavities of these chains. (8)
- 27. Substance having lowest boiling point. (6)



CHEMISTRY TODAY | DECEMBER '15



Now, save up to Rs 2,020*











Subscribe to MTG magazines today.

Our 2015 offers are here. Pick the combo best suited for your needs. Fill-in the Subscription Form at the bottom and mail it to us today. If in a rush, log on to www.mtg.in now to subscribe online.

*On cover price of ₹ 30/- each.

About MTG's Magazines

For JEE (Main & Advanced), AIPMT, PMTs, All State Level Engg. & **Medical Exams**

Perfect for students who like to prepare at a steady pace, MTG's magazines - Physics For You, Chemistry

Today, Mathematics Today & Biology Today - ensure you practice bit by bit, month by month, to build all-round command over key subjects. Did you know these magazines are the only source for solved test papers of all national and state level engineering and medical college entrance exams?

Trust of over 1 Crore readers. Since 1982.

- · Practice steadily, paced month by month, with very-similar & model test papers
- Self-assessment tests for you to evaluate your readiness and confidence for the big exams
- Content put together by a team
- comprising experts and members from MTG's well-experienced **Editorial Board**
- Stay up-to-date with important information such as examination dates, trends & changes in syllabi
- All-round skill enhancement –

confidence-building exercises, new studying techniques, time management, even advice from past IIT/PMT toppers

 Bonus: exposure to competition at a global level, with guestions from Intl. Olympiads & Contests

Please accept my subscription to: (Confirm your choice by ticking the appropriate boxes)	Name:
PCMB combo	Complete Postal Address:
	s: ₹ 2,300 e ₹ 2,020)
PCM combo	1
	s: ₹ 1,900 e ₹ 1,340) Pin Code Mobile #
PCB combo	
	s: ₹ 1,900 Other Phone # 0
Individual magazines	Email
Physics Chemistry Mathematics	Biology Enclose Demand Draft favouring MTG Learning Media (P) Ltd, payable at New
	Delhi, You can also pay via Money Orders. Mail this Subscription Form to Subscription Dept., MTG Learning Media (P) Ltd, Plot 99, Sector 44, Gurgaon – 122 003 (HR).
	th of every month (each magazine separately). Should you want us to send you your copies by al charges apply (₹ 240, ₹ 450, ₹ 600 for 1-yr, 2-yr, 3-yr subscriptions respectively).
PLANE DEPENDENT OF THE PLANE AND THE PLANE A	w.mta.in to subscribe online. Call (0)8800255334/5 for more info.

