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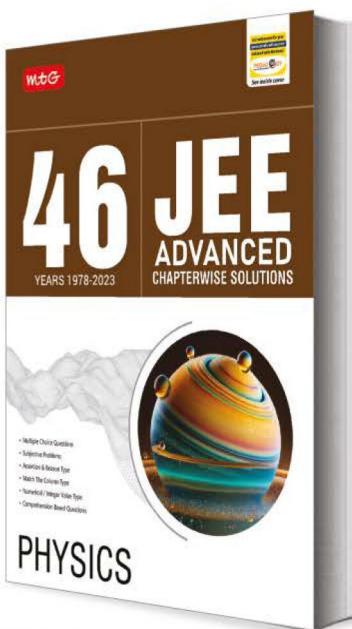
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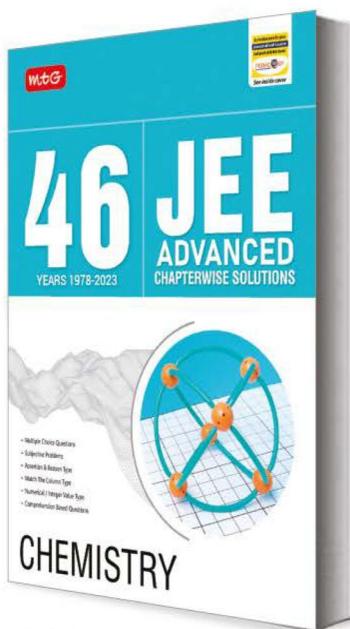
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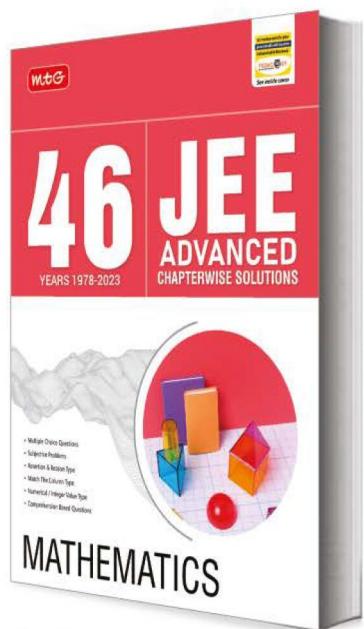
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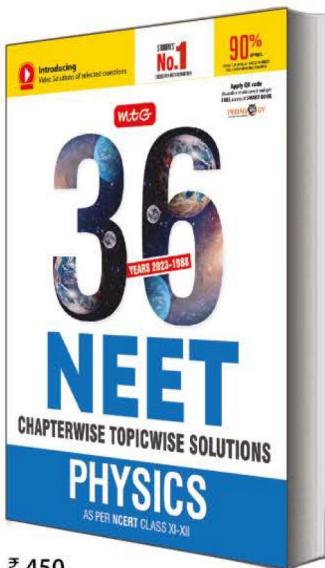


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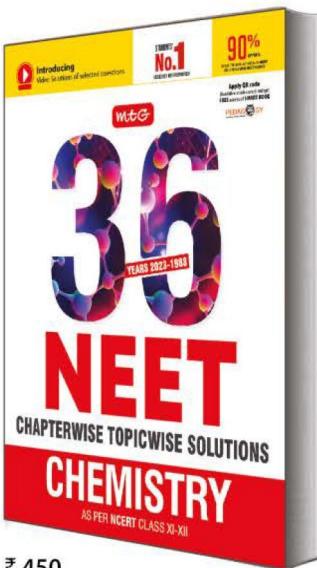
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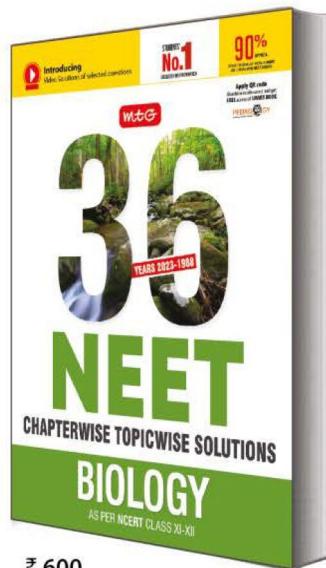
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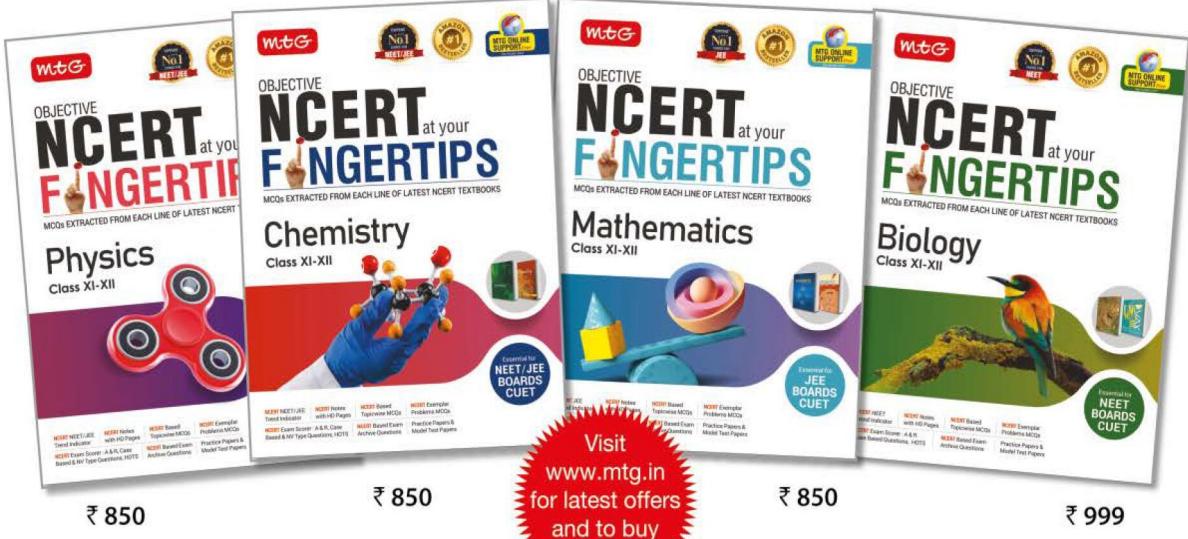
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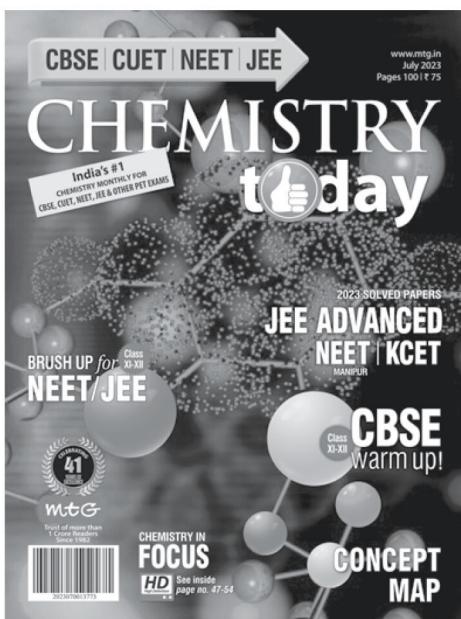
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JEE ADVANCED 2023

SOLVED PAPER



PAPER-I

SECTION 1 (MAXIMUM MARKS : 12)

- This section contains THREE (03) questions.*
- Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct answer(s).*
- For each question, choose the option(s) corresponding to (all) the correct answer(s).*
- Answer to each question will be evaluated according to the following marking scheme:*

Full Marks : +4 ONLY if (all) the correct option(s) is(are) chosen;

Partial Marks : +3 If all the four options are correct but ONLY three options are chosen;

Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct;

Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option;

Zero Marks : 0 If none of the options is chosen (i.e., the question is unanswered);

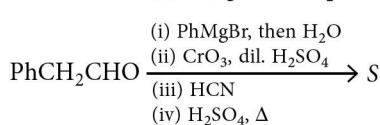
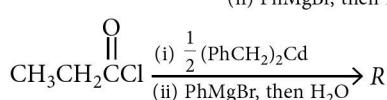
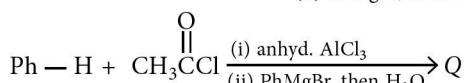
Negative Marks : -2 In all other cases.

- For example, in a question, if (a), (b) and (d) are the ONLY three options corresponding to correct answers, then choosing ONLY (a), (b) and (d) will get +4 marks; choosing ONLY (a) and (b) will get +2 marks; choosing ONLY (a) and (d) will get +2 marks; choosing ONLY (b) and (d) will get +2 marks; choosing ONLY (a) will get +1 mark; choosing ONLY (b) will get +1 mark; choosing ONLY (d) will get +1 mark; choosing no option (i.e., the question is unanswered) will get 0 marks; and choosing any other combination of options will get -2 marks.*

- The correct statement(s) related to processes involved in the extraction of metals is (are)
 - roasting of malachite produces cuprite
 - calcination of calamine produces zincite

- (c) copper pyrites is heated with silica in a reverberatory furnace to remove iron
 (d) impure silver is treated with aqueous KCN in the presence of oxygen followed by reduction with zinc metal.

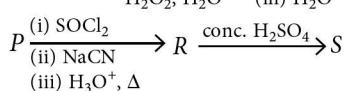
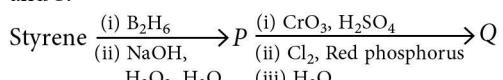
- In the following reactions, P, Q, R, and S are the major products.

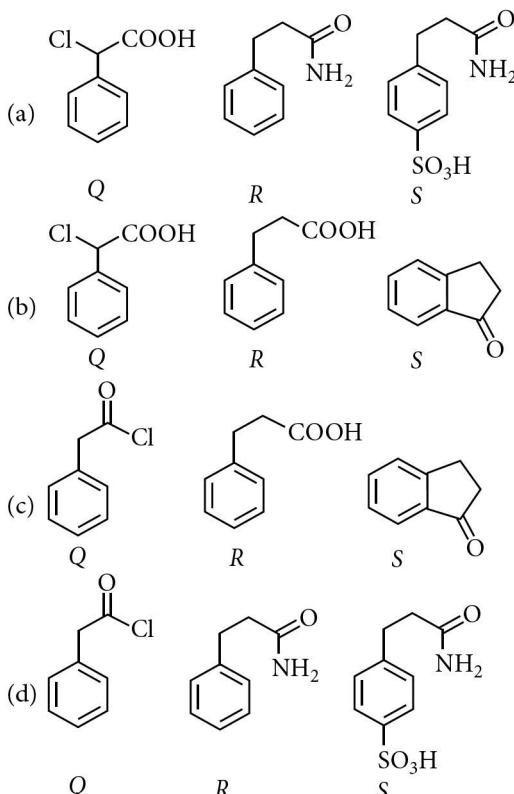


The correct statement(s) about P, Q, R, and S is(are)

- Both P and Q have asymmetric carbon(s).
- Both Q and R have asymmetric carbon(s).
- Both P and R have asymmetric carbon(s).
- P has asymmetric carbon(s), S does not have any asymmetric carbon.

- Consider the following reaction scheme and choose the correct option(s) for the major products Q, R and S.

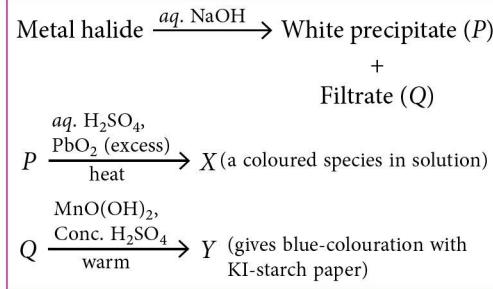




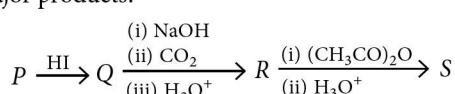
SECTION 2 (MAXIMUM MARKS : 12)

- This section contains FOUR (04) questions.*
- Each question has FOUR options (a), (b), (c) and (d). Only one of these four option is the correct answer.*
- For each question, choose the option corresponding to the correct answer.*
- Answer to each question will be evaluated according to the following marking scheme:*
 Full Marks : +3 If ONLY the correct option is chosen;
 Zero Marks : 0 If none of the options is chosen (i.e., the question is unanswered);
 Negative Marks : -1 In all other cases.

4. In the scheme given below, X and Y, respectively, are



- (a) CrO_4^{2-} and Br_2 (b) MnO_4^{2-} and Cl_2
 (c) MnO_4^- and Cl_2 (d) MnSO_4 and HOCl
5. Plotting $1/\Lambda_m$ against $c\Lambda_m$ for aqueous solutions of a monobasic weak acid (HX) resulted in a straight line with y -axis intercept of P and slope of S . The ratio P/S is
 [Λ_m = molar conductivity, Λ_m° = limiting molar conductivity, c = molar concentration, K_a = dissociation constant of HX]
 (a) $K_a \Lambda_m^\circ$ (b) $K_a \Lambda_m^\circ/2$
 (c) $2K_a \Lambda_m^\circ$ (d) $1/(K_a \Lambda_m^\circ)$
6. On decreasing the pH from 7 to 2, the solubility of a sparingly soluble salt (MX) of a weak acid (HX) increased from 10^{-4} mol L⁻¹ to 10^{-3} mol L⁻¹. The $\text{p}K_a$ of HX is
 (a) 3 (b) 4 (c) 5 (d) 2
7. In the given reaction scheme, P is a phenyl alkyl ether, Q is an aromatic compound; R and S are the major products.



The correct statement about S is

- It primarily inhibits noradrenaline degrading enzymes.
- It inhibits the synthesis of prostaglandin.
- It is a narcotic drug.
- It is *ortho*-acetylbenzoic acid.

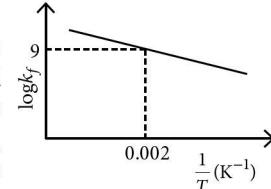
SECTION 3 (MAXIMUM MARKS : 24)

- This section contains SIX (06) questions.*
 - The answer to each question is a NON-NEGATIVE INTEGER.*
 - For each question, enter the correct integer corresponding to the answer using the mouse and the onscreen virtual numeric keypad in the place designated to enter the answer.*
 - Answer to each question will be evaluated according to the following marking scheme:*
 Full Marks : +4 If ONLY the correct integer is entered;
 Zero Marks : 0 In all other cases.
8. The stoichiometric reaction of 516 g of dimethyl-dichlorosilane with water results in a tetrmeric cyclic product X in 75% yield. The weight (in g) of X obtained is ____.
 [Use, molar mass (g mol⁻¹): H = 1, C = 12, O = 16, Si = 28, Cl = 35.5]

9. A gas has a compressibility factor of 0.5 and a molar volume of $0.4 \text{ dm}^3 \text{ mol}^{-1}$ at a temperature of 800 K and pressure $x \text{ atm}$. If it shows ideal gas behaviour at the same temperature and pressure, the molar volume will be $y \text{ dm}^3 \text{ mol}^{-1}$. The value of x/y is _____. [Use: Gas constant, $R = 8 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$]

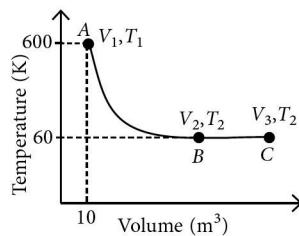
10. The plot of $\log k_f$ versus $1/T$ for a reversible reaction $A_{(g)} \rightleftharpoons P_{(g)}$ is shown.

Pre-exponential factors for the forward and backward reactions are 10^{15} s^{-1} and 10^{11} s^{-1} , respectively. If the value of $\log K$ for the reaction at 500 K is 6, the value of $|\log k_b|$ at 250 K is _____. [K = equilibrium constant of the reaction, k_f = rate constant of forward reaction, k_b = rate constant of backward reaction]



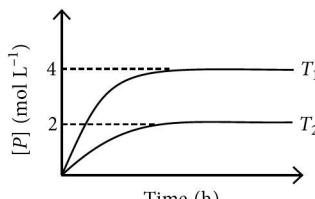
11. One mole of an ideal monoatomic gas undergoes two reversible processes ($A \rightarrow B$ and $B \rightarrow C$) as shown in the given figure:

$A \rightarrow B$ is an adiabatic process. If the total heat absorbed in the entire process ($A \rightarrow B$ and $B \rightarrow C$) is $RT_2 \ln 10$, the value of $2 \log V_3$ is _____. [Use, molar heat capacity of the gas at constant pressure, $C_{p,m} = \frac{5}{2} R$]

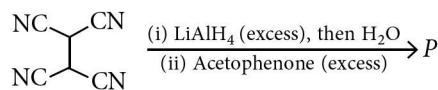


12. In a one-litre flask, 6 moles of A undergoes the reaction, $A_{(g)} \rightleftharpoons P_{(g)}$. The progress of product formation at two temperatures (in Kelvin), T_1 and T_2 , is shown in the figure :

If $T_1 = 2T_2$ and $(\Delta G_2^\circ - \Delta G_1^\circ) = RT_2 \ln x$, then the value of x is _____. [ΔG_1° and ΔG_2° are standard Gibbs free energy change for the reaction at temperatures T_1 and T_2 , respectively.]



13. The total number of sp^2 hybridised carbon atoms in the major product P (a non-heterocyclic compound) of the following reaction is _____.



SECTION 4 (MAXIMUM MARKS : 12)

- This section contains FOUR (04) Matching List Sets..
- Each set has ONE Multiple Choice Question.
- Each set has TWO lists : List-I and List-II.
- List-I has Four entries (P), (Q), (R) and (S) and List-II has Five entries (1), (2), (3), (4) and (5).
- FOUR options are given in each Multiple Choice Question based on List-I and List-II and ONLY ONE of these four options satisfies the condition asked in the Multiple Choice Question.
- Answer to each question will be evaluated according to the following marking scheme:
Full Marks : +3 ONLY if the option corresponding to the correct combination is chosen;
Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered);
Negative Marks : -1 In all other cases.

14. Match the reactions (in the given stoichiometry of the reactants) in List-I with one of their products given in List-II and choose the correct option.

List-I		List-II	
(P)	$\text{P}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow$	1.	$\text{P}(\text{O})(\text{OCH}_3)\text{Cl}_2$
(Q)	$\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow$	2.	H_3PO_3
(R)	$\text{PCl}_5 + \text{CH}_3\text{COOH} \rightarrow$	3.	PH_3
(S)	$\text{H}_3\text{PO}_2 + 2\text{H}_2\text{O} + 4\text{AgNO}_3 \rightarrow$	4.	POCl_3
		5.	H_3PO_4

- (a) P \rightarrow 2; Q \rightarrow 3; R \rightarrow 1; S \rightarrow 5
 (b) P \rightarrow 3; Q \rightarrow 5; R \rightarrow 4; S \rightarrow 2
 (c) P \rightarrow 5; Q \rightarrow 2; R \rightarrow 1; S \rightarrow 3
 (d) P \rightarrow 2; Q \rightarrow 3; R \rightarrow 4; S \rightarrow 5

15. Match the electronic configurations in List-I with appropriate metal complex ions in List-II and choose the correct option.

[Atomic Number: Fe = 26, Mn = 25, Co = 27]

List-I		List-II	
(P)	$t_{2g}^6 e_g^0$	1.	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
(Q)	$t_{2g}^3 e_g^2$	2.	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
(R)	$e^2 t_2^3$	3.	$[\text{Co}(\text{NH}_3)_6]^{3+}$
(S)	$t_{2g}^4 e_g^2$	4.	$[\text{FeCl}_4]^-$
		5.	$[\text{CoCl}_4]^{2-}$

- (a) P → 1; Q → 4; R → 2; S → 3
 (c) P → 3; Q → 2; R → 5; S → 1
- (b) P → 1; Q → 2; R → 4; S → 5
 (d) P → 3; Q → 2; R → 4; S → 1

16. Match the reactions in List-I with the features of their products in List-II and choose the correct option.

List-I		List-II	
(P)	(-) -1-Bromo-2-ethylpentane $\xrightarrow[\text{S}_{\text{N}}2 \text{ reaction}]{\text{aq. NaOH}}$ (single enantiomer)	1.	Inversion of configuration
(Q)	(-) -2-Bromopentane $\xrightarrow[\text{S}_{\text{N}}2 \text{ reaction}]{\text{aq. NaOH}}$ (single enantiomer)	2.	Retention of configuration
(R)	(-) -3-Bromo-3-methylhexane $\xrightarrow[\text{S}_{\text{N}}1 \text{ reaction}]{\text{aq. NaOH}}$ (single enantiomer)	3.	Mixture of enantiomers
(S)	 $\xrightarrow[\text{S}_{\text{N}}1 \text{ reaction}]{\text{aq. NaOH}}$ (single enantiomer)	4.	Mixture of structural isomers
		5.	Mixture of diastereomers

- (a) P → 1; Q → 2; R → 5; S → 3
 (b) P → 2; Q → 1; R → 3; S → 5
 (c) P → 1; Q → 2; R → 5; S → 4
 (d) P → 2; Q → 4; R → 3; S → 5

17. The major products obtained from the reactions in List-II are the reactants for the named reactions mentioned in List-I. Match List-I with List-II and choose the correct option.

List-I		List-II	
(P)	Etard reaction	1.	Acetophenone $\xrightarrow[\text{HCl}]{\text{Zn-Hg}}$
(Q)	Gattermann reaction	2.	Toluene $\xrightarrow[\text{(ii) SOCl}_2]{\text{(i) KMnO}_4, \text{ KOH, } \Delta}$
(R)	Gattermann-Koch reaction	3.	Benzene $\xrightarrow[\text{anhyd. AlCl}_3]{\text{CH}_3\text{Cl}}$
(S)	Rosenmund reduction	4.	Aniline $\xrightarrow[\text{273-278 K}]{\text{NaNO}_2/\text{HCl}}$
		5.	Phenol $\xrightarrow{\text{Zn, } \Delta}$

- (a) P → 2; Q → 4; R → 1; S → 3
 (b) P → 1; Q → 3; R → 5; S → 2
 (c) P → 3; Q → 2; R → 1; S → 4
 (d) P → 3; Q → 4; R → 5; S → 2

PAPER - II

SECTION 1 (MAXIMUM MARKS : 12)

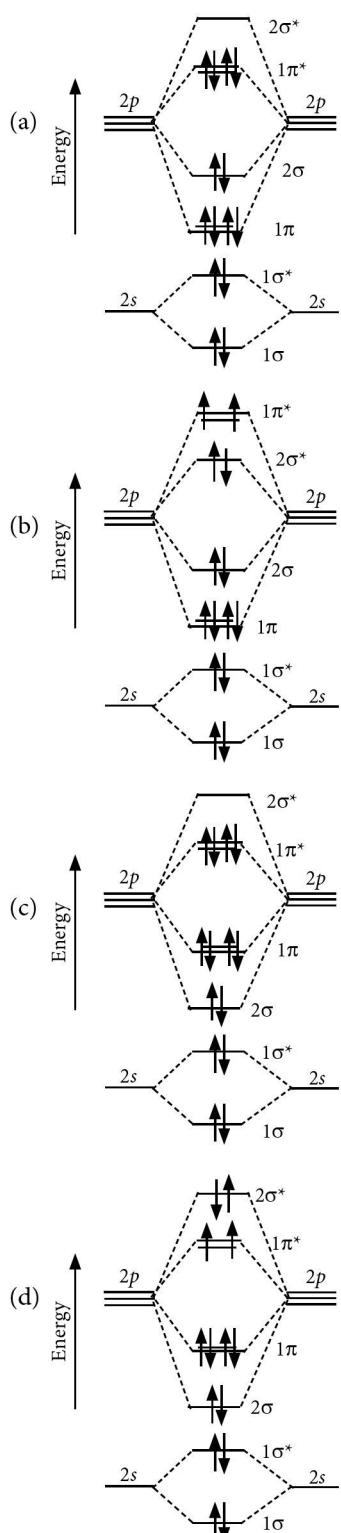
- This section contains FOUR (04) questions.
- Each question has FOUR options (a), (b), (c) and (d). Only one of these four options is the correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +3 If ONLY the correct option is chosen;

Zero Marks : 0 If none of the options is chosen (i.e., the question is unanswered);

Negative Marks : -1 In all other cases.

1. The correct molecular orbital diagram for F₂ molecule in the ground state is



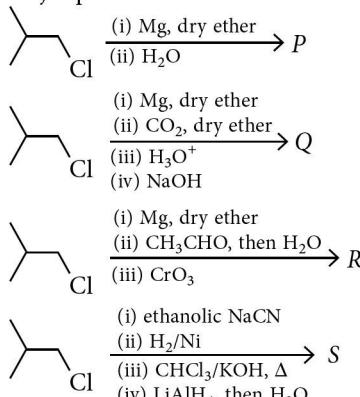
2. Consider the following statements related to colloids.

- (I) Lyophobic colloids are not formed by simple mixing of dispersed phase and dispersion medium.
- (II) For emulsions, both the dispersed phase and the dispersion medium are liquid.
- (III) Micelles are produced by dissolving a surfactant in any solvent at any temperature.
- (IV) Tyndall effect can be observed from a colloidal solution with dispersed phase having the same refractive index as that of the dispersion medium.

The option with the correct set of statements is

- | | |
|--------------------|--------------------|
| (a) (I) and (II) | (b) (II) and (III) |
| (c) (III) and (IV) | (d) (II) and (IV). |

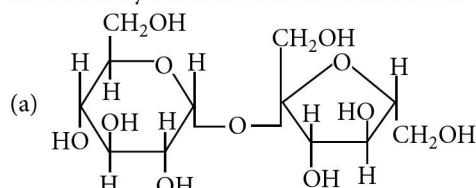
3. In the following reactions, P, Q, R, and S are the major products.

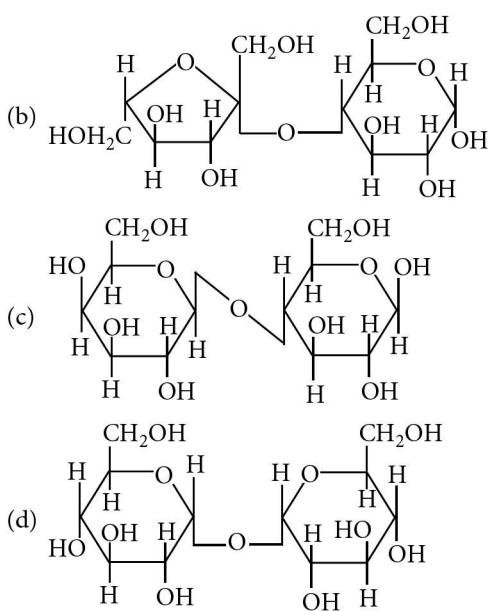


The correct statement about P, Q, R, and S is

- (a) P is a primary alcohol with four carbons.
- (b) Q undergoes Kolbe's electrolysis to give an eight-carbon product.
- (c) R has six carbons and it undergoes Cannizzaro reaction.
- (d) S is a primary amine with six carbons.

4. A disaccharide X cannot be oxidised by bromine water. The acid hydrolysis of X leads to a laevorotatory solution. The disaccharide X is





SECTION 2 (MAXIMUM MARKS : 12)

- This section contains THREE (03) questions.*
 - Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct answer(s).*
 - For each question, choose the option(s) corresponding to (all) the correct answer(s).*
 - Answer to each question will be evaluated according to the following marking scheme:*
- Full Marks** : +4 ONLY if (all) the correct option(s) is(are) chosen;
- Partial Marks** : +3 If all the four options are correct but ONLY three options are chosen;
- Partial Marks** : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct;
- Partial Marks** : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option;
- Zero Marks** : 0 If unanswered;
- Negative Marks** : -2 In all other cases.
- For example, in a question, if (a), (b) and (c) are the ONLY three options corresponding to correct answers, then choosing ONLY (a), (b) and (d) will get +4 marks; choosing ONLY (a) and (b) will get +2 marks; choosing ONLY (a) and (d) will get +2 marks; choosing ONLY (b) and (d) will get +2 marks; choosing ONLY (a) will get +1 mark; choosing ONLY (b) will get +1 mark; choosing ONLY (d) will get +1 mark; choosing no option(s) (i.e., the question is unanswered) will get 0 marks; and choosing any other option(s) will get -2 marks.*

5. The complex(es), which can exhibit the type of isomerism shown by $[\text{Pt}(\text{NH}_3)_2\text{Br}_2]$, is(are) $[\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2]$

(a) $[\text{Pt}(\text{en})(\text{SCN})_2]$ (b) $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$
 (c) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ (d) $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})(\text{SO}_4)]^+$

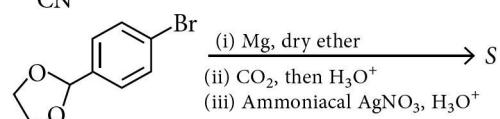
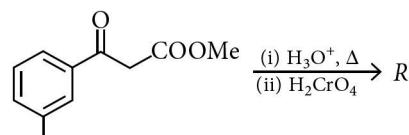
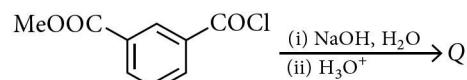
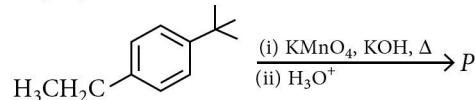
6. Atoms of metals x , y and z form face-centred cubic (*fcc*) unit cell of edge length L_x , body-centred cubic (*bcc*) unit cell of edge length L_y and simple cubic unit cell of edge length L_z , respectively.

If $r_z = \frac{\sqrt{3}}{2}r_y$; $r_y = \frac{8}{\sqrt{3}}r_x$; $M_z = \frac{3}{2}M_y$ and $M_z = 3M_x$, then the correct statement(s) is(are)

[Given: M_x , M_y and M_z are molar masses of metals x , y and z , respectively. r_x , r_y and r_z are atomic radii of metals x , y and z , respectively.]

- (a) Packing efficiency of unit cell of x > Packing efficiency of unit cell of y > Packing efficiency of unit cell of z
 (b) $L_y > L_z$
 (c) $L_x > L_y$
 (d) Density of x > Density of y

7. In the following reactions, P , Q , R and S are the major products.



The correct statement(s) about P , Q , R and S is(are)

- (a) P and Q are monomers of polymers dacron and glyptal, respectively.
 (b) P , Q and R are dicarboxylic acids.
 (c) Compounds Q and R are the same.
 (d) R does not undergo aldol condensation and S does not undergo Cannizzaro reaction.

SECTION 3 (MAXIMUM MARKS : 24)

- This section contains SIX (06) questions.
- The answer to each question is a NON-NEGATIVE INTEGER.
- For each question, enter the correct integer corresponding to the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 If ONLY the correct integer is entered;

Zero Marks : 0 In all other cases.

8. H_2S (5 moles) reacts completely with acidified aqueous potassium permanganate solution. In this reaction, the number of moles of water produced is x , and the number of moles of electrons involved is y . The value of $(x + y)$ is ____.
9. Among $[\text{I}_3]^+$, $[\text{SiO}_4]^{4-}$, SO_2Cl_2 , XeF_2 , SF_4 , ClF_3 , $\text{Ni}(\text{CO})_4$, XeO_2F_2 , $[\text{PtCl}_4]^{2-}$, XeF_4 , and SOCl_2 , the total number of species having sp^3 hybridised central atom is ____.
10. Consider the following molecules: Br_3O_8 , F_2O , $\text{H}_2\text{S}_4\text{O}_6$, $\text{H}_2\text{S}_5\text{O}_6$ and C_3O_2 . Count the number of atoms existing in their zero oxidation state in each molecule. Their sum is ____.
11. For He^+ , a transition takes place from the orbit of radius 105.8 pm to the orbit of radius 26.45 pm. The wavelength (in nm) of the emitted photon during the transition is ____.
[Use: Bohr radius, $a = 52.9 \text{ pm}$
Rydberg constant, $R_H = 2.2 \times 10^{-18} \text{ J}$
Planck's constant, $h = 6.6 \times 10^{-34} \text{ J s}$
Speed of light, $c = 3 \times 10^8 \text{ m s}^{-1}$]

12. 50 mL of 0.2 molal urea solution (density = 1.012 g mL^{-1} at 300 K) is mixed with 250 mL of a solution containing 0.06 g of urea. Both the solutions were prepared in the same solvent. The osmotic pressure (in Torr) of the resulting solution at 300 K is ____.
[Use: Molar mass of urea = 60 g mol^{-1} ; gas constant, $R = 62 \text{ L Torr K}^{-1} \text{ mol}^{-1}$; Assume, $\Delta_{\text{mix}}H = 0$, $\Delta_{\text{mix}}V = 0$]

13. The reaction of 4-methyloct-1-ene (P , 2.52 g) with HBr in the presence of $(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$ gives two isomeric bromides in a 9 : 1 ratio, with a combined yield of 50%. Of these, the entire amount of the primary alkyl bromide was reacted with

an appropriate amount of diethylamine followed by treatment with *aq.* K_2CO_3 to give a non-ionic product S in 100% yield. The mass (in mg) of S obtained is ____.

[Use molar mass (in g mol^{-1}): H = 1, C = 12, N = 14, Br = 80]

SECTION 4 (MAXIMUM MARKS : 12)

- This section contains TWO (02) paragraphs.
- Based on each paragraph, there are TWO (02) questions.
- The answer to each question is a NUMERICAL VALUE.
- For each question, enter the correct numerical value of the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
- If the numerical value has more than two decimal places, truncate/round-off the value to TWO decimal places.
- Answer to each question will be evaluated according to the following marking scheme:

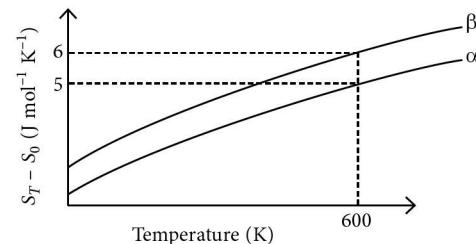
Full Marks : +3 If ONLY the correct numerical value is entered in the designated place;

Zero Marks : 0 In all other cases.

PARAGRAPH-I

The entropy versus temperature plot for phases α and β at 1 bar pressure is given.

S_T and S_0 are entropies of the phases at temperatures T and 0 K, respectively.



The transition temperature for α to β phase change is 600 K and $C_{p,\beta} - C_{p,\alpha} = 1 \text{ J mol}^{-1} \text{ K}^{-1}$. Assume $(C_{p,\beta} - C_{p,\alpha})$ is independent of temperature in the range of 200 to 700 K. $C_{p,\alpha}$ and $C_{p,\beta}$ are heat capacities of α and β phases, respectively.

14. The value of entropy change, $S_\beta - S_\alpha$ (in $\text{J mol}^{-1} \text{ K}^{-1}$), at 300 K is ____.

[Use: $\ln 2 = 0.69$. Given: $S_\beta - S_\alpha = 0$ at 0 K]

15. The value of enthalpy change, $H_\beta - H_\alpha$ (in J mol^{-1}), at 300 K is ____.

PARAGRAPH-II

A trinitro compound, 1,3,5-tris-(4-nitrophenyl)benzene, on complete reaction with an excess of Sn/HCl gives a

major product, which on treatment with an excess of NaNO_2/HCl at 0°C provides P as the product. P , upon treatment with excess of H_2O at room temperature, gives the product Q . Bromination of Q in aqueous medium furnishes the product R . The compound P upon treatment with an excess of phenol under basic conditions gives the product S .

The molar mass difference between compounds Q and R is 474 g mol^{-1} and between compounds P and S is 172.5 g mol^{-1} .

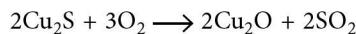
- 16.** The number of heteroatoms present in one molecule of R is _____.
[Use: Molar mass (in g mol^{-1}): H = 1, C = 12, N = 14, O = 16, Br = 80, Cl = 35.5. Atoms other than C and H are considered as heteroatoms]

- 17.** The total number of carbon atoms and heteroatoms present in one molecule of S is _____.
[Use: Molar mass (in g mol^{-1}): H = 1, C = 12, N = 14, O = 16, Br = 80, Cl = 35.5. Atoms other than C and H are considered as heteroatoms]

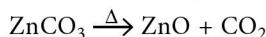
SOLUTIONS

PAPER-I

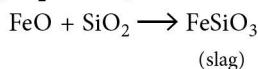
- 1. (b, c, d) :** Statement (a) is incorrect as roasting of copper glance (Cu_2S) produces cuprite (Cu_2O) as shown :



Statement (b) is correct as calcination of calamine (ZnCO_3) produces zincite (ZnO) as shown :

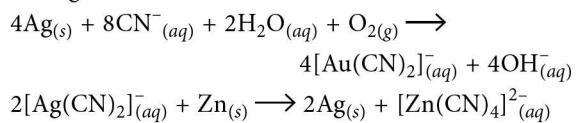


Statement (c) is true as the copper ore (copper pyrite) is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags off' as iron silicate is formed. Copper is produced in the form of copper matte ($\text{Cu}_2\text{S} + \text{FeS}$).



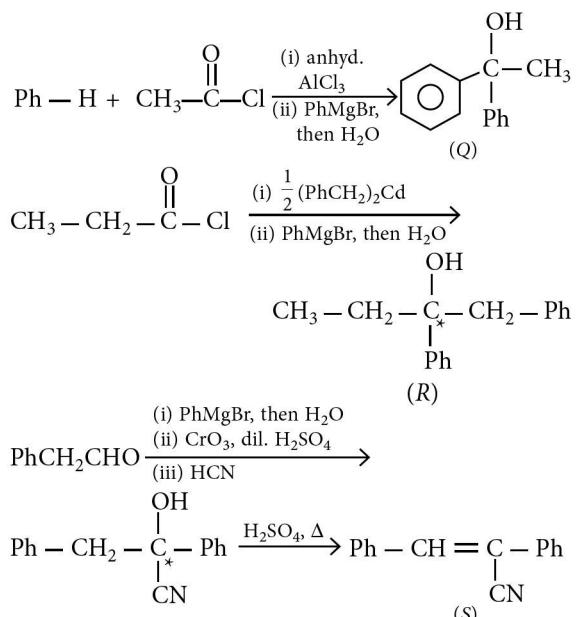
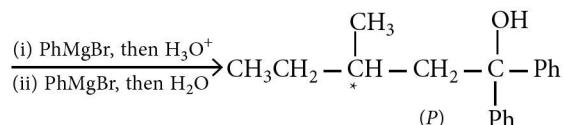
Copper matte is then discharged into silica lined converter. Some silica is also added and hot air blast is blown to convert the remaining FeS , FeO and $\text{Cu}_2\text{S}/\text{Cu}_2\text{O}$ to the metallic copper.

Statement (d) is correct as the following reactions occur during extraction of silver.

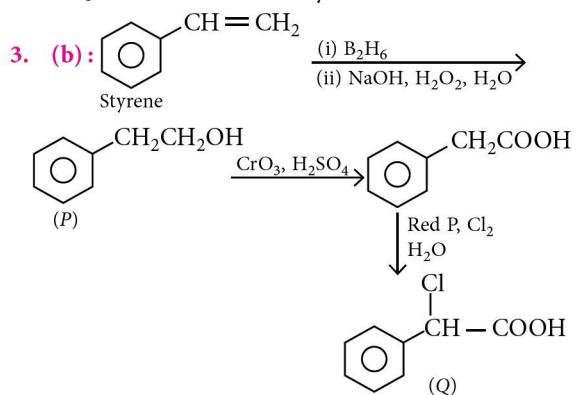


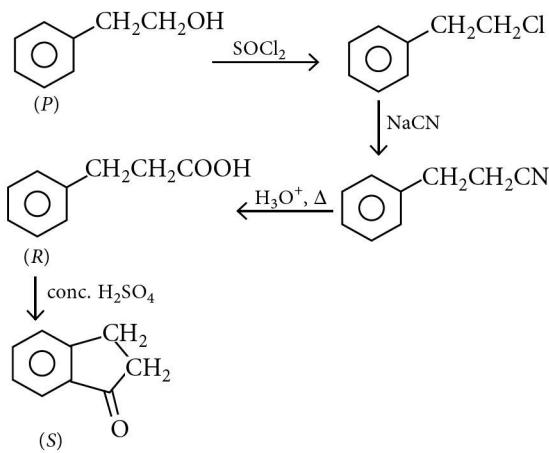
Hence, (b, c, d) are correct.

- 2. (c, d) :** $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CN}$

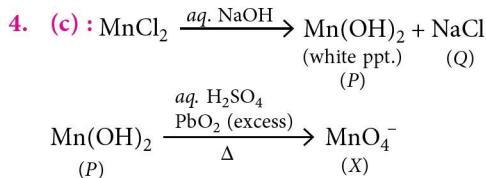


Hence, products P and R have asymmetric carbon atoms, while Q and S do not have asymmetric carbon atoms.

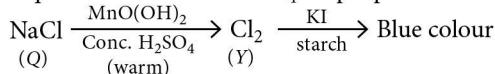




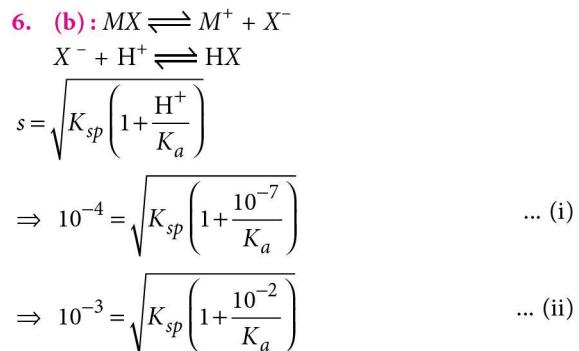
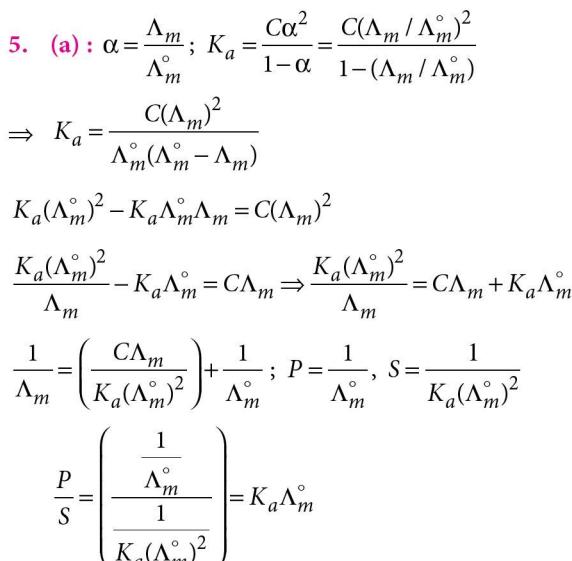
Hence, the correct option is (b).



The aqueous solution of MnO_4^- is purple in colour.



Chlorine is placed below iodine in the electrochemical series and has a higher reduction potential than iodine. Thus, chlorine undergoes reduction while I^- undergoes oxidation. I_2 so produced gets absorbed in starch to give blue colour.



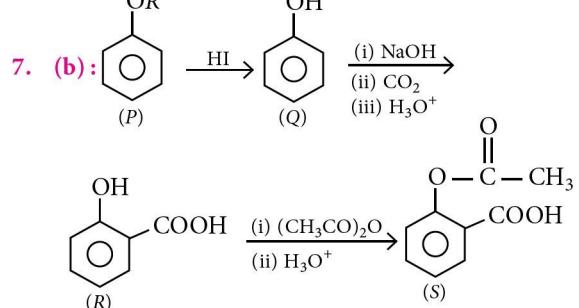
Divide eq. (i) by eq. (ii),

$$10^{-2} = \frac{\left(1 + \frac{10^{-7}}{K_a}\right)}{\left(1 + \frac{10^{-2}}{K_a}\right)} \Rightarrow 10^{-2} + \frac{10^{-4}}{K_a} = 1 + \frac{10^{-7}}{K_a}$$

$$\frac{10^{-4} - 10^{-7}}{K_a} = 0.99 \Rightarrow \frac{10^{-4}}{K_a} = 0.99 \quad (\because 10^{-7} \ll 10^{-4})$$

$$K_a = \frac{10^{-4}}{0.99} \Rightarrow K_a = 10^{-4} \quad (\because 0.99 \approx 1)$$

$$pK_a = 4$$



The compound *S* is *ortho*-acetoxybenzoic acid (aspirin) and it inhibits the synthesis of prostaglandin.

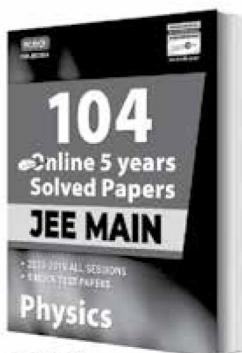
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JUNE 2023

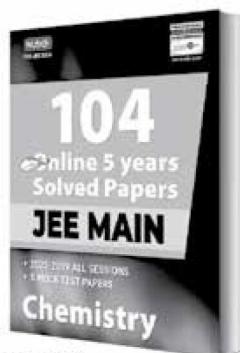
- | | |
|------------------------|-------------------|
| 1-c- LIMONITE | 2-d- PHOTOLYSIS |
| 3-a- OSMOMETER | 4-b- SPECTROGRAPH |
| 5-f- TRITIUM | 6-e- YTTERBIUM |
| 7-i- SUPERCONDUCTIVITY | 8-g- CHLOROPICRIN |
| 9-h- KEVLAR | 10-j-TEFLON |

Winners: Kaushikkumar Kevadiya, Sourish Dhara

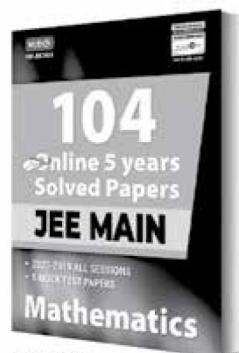
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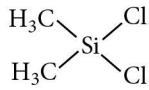
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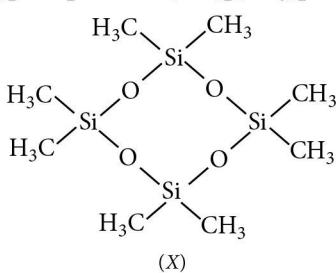
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8. (222) : The structure of dimethyldichlorosilane is as follows :



Mol. mass - 129 g/mol

Number of moles of dimethyldichlorosilane initially taken = $\frac{516 \text{ g}}{129 \text{ g mol}^{-1}} = 4 \text{ mol}$



Applying principle of atom conservation (POAC) on Si atom,

$$\text{moles of tetrameric cyclic product (X) formed} = \frac{4}{4} \times \frac{75}{100} = 0.75 \text{ mol}$$

Molar mass of product (X) formed = 296 g mol⁻¹

The mass of product (X) formed

$$= 296 \text{ g mol}^{-1} \times 0.75 \text{ mol} = 222 \text{ g}$$

9. (100) : Compressibility factor (*Z*) = $\frac{V_{\text{real}}}{V_{\text{ideal}}} = 0.5$

$$V_{\text{real}} = 0.4 \text{ dm}^3 \text{ mol}^{-1} = 0.4 \text{ L mol}^{-1}$$

$$V_{\text{ideal}} = \frac{0.4}{0.5} = 0.8 \text{ L/mol} ; y = 0.8 \text{ L/mol}$$

Using ideal gas equation, $PV = nRT$

$$P = \frac{1 \times 8 \times 10^{-2} \times 800}{0.8} ; x = 80 \text{ atm}$$

$$\text{Thus, } \frac{x}{y} = \frac{80}{0.8} = 100$$

10. (5) : From the given problem,

$$A_f = 10^{15} \text{ s}^{-1}, A_b = 10^{11} \text{ s}^{-1}$$

f = forward reaction, *b* = backward reaction

logK at 500 K = 6

logk_f at 500 K = 9 (from graph)

To find *logk_b* at 500 K,

$$\log K = \log \left(\frac{k_f}{k_b} \right) \quad \left(\because K = \frac{k_f}{k_b} \right)$$

$$6 = \log k_f - \log k_b \Rightarrow 6 = 9 - \log k_b$$

logk_b = 3 at 500 K

$$\text{To find } E_a, k_b = A_b e^{\frac{-E_a}{RT}}$$

$$\ln k_b = \ln \left(A_b e^{\frac{-E_a}{RT}} \right) \text{ or } \ln k_b = \ln A_b - \frac{E_a}{RT}$$

$$2.303 \log k_b = 2.303 \log A_b - \frac{E_a}{500R}$$

$$\frac{E_a}{500R} = 2.303(\log A_b - \log k_b)$$

$$\frac{E_a}{500R} = 2.303(\log 10^{11} - 3)$$

$$\frac{E_a}{500R} = 2.303(11 - 3) = 2.303 \times 8$$

$$E_a = 2.303 \times 8 \times 500R$$

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Rightarrow \ln \left(\frac{k_{b_{250 \text{ K}}}}{k_{b_{500 \text{ K}}}} \right) = \frac{-E_a}{R} \left(\frac{1}{250} - \frac{1}{500} \right)$$

$$\Rightarrow \ln \left(\frac{k_{b_{250 \text{ K}}}}{k_{b_{500 \text{ K}}}} \right) = \frac{-2.303 \times 8 \times 500R}{R} \left(\frac{1}{500} \right)$$

$$\Rightarrow 2.303(\log k_{b_{250 \text{ K}}} - \log k_{b_{500 \text{ K}}}) = -2.303 \times 8$$

$$\Rightarrow \log k_{b_{250 \text{ K}}} - 3 = -8 \Rightarrow \log k_{b_{250 \text{ K}}} = -5$$

Hence, $|\log k_{b_{250 \text{ K}}}| = 5$

11. (7) : It has been mentioned in the problem that

$$q_{A \rightarrow C} = RT_2 \ln 10$$

$$q_{A \rightarrow B} = 0 \quad (\because \text{adiabatic process})$$

$$q_{A \rightarrow C} = q_{A \rightarrow B} + q_{B \rightarrow C}$$

$$q_{A \rightarrow C} = q_{B \rightarrow C}$$

$$q_{A \rightarrow C} = nRT_2 \ln \left(\frac{V_3}{V_2} \right) \quad \dots (i)$$

$$\text{For } B \rightarrow C, \Delta E = q + w$$

$$\Delta E = 0 \quad (\because \text{isothermic process})$$

Quotable Quote 99

Success can only come to you by courageous devotion
to the task lying in front of you.

C. V. Raman

$$q = -w = -\left(-nRT_2 \ln \frac{V_3}{V_2}\right) = nRT_2 \ln \left(\frac{V_3}{V_2}\right)$$

$$q_{B \rightarrow C} = nRT_2 \ln \left(\frac{V_3}{V_2}\right)$$

$$q_{B \rightarrow C} = RT_2 \ln \left(\frac{V_3}{V_2}\right) \quad (\text{As } n = 1)$$

$$\text{From } A \rightarrow B, T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$600V_1^{\gamma-1} = 60V_2^{\gamma-1} \Rightarrow 10 \times 10^3^{\frac{5}{3}-1} = V_2^{\gamma-1}$$

(for monoatomic gas, $\gamma = 5/3$)

$$10^{5/3} = V_2^{\frac{5}{3}-1} \Rightarrow 10^{5/3} = V_2^{2/3}$$

$$\Rightarrow V_2 = 10^3^{\frac{5 \times 3}{2}} = 10^{\frac{5}{2}} \Rightarrow V_2 = 10^{5/2} \quad \dots \text{(ii)}$$

$$\text{From eq. (i), } q_{A \rightarrow C} = nRT_2 \ln \left(\frac{V_3}{V_2}\right)$$

$$RT_2 \ln 10 = RT_2 \ln \left(\frac{V_3}{V_2}\right)$$

$$\Rightarrow \ln 10 = \ln \left(\frac{V_3}{V_2}\right) \Rightarrow \ln 10 = \ln \left(\frac{V_3}{10^{5/2}}\right)$$

$$\Rightarrow V_3 = 10^{\frac{1+5}{2}} = 10^{\frac{7}{2}}$$

$$2 \log V_3 = 2 \log 10^{7/2} = 7$$

12. (8): $A_{(g)} \rightleftharpoons P_{(g)}$

Initially

6

0

At equilibrium

$6 - a$

a

$$\text{At } T_1, a = 4 \quad \therefore (K_{\text{eq}})_1 = \frac{4}{2} = 2$$

$$\text{at } T_2, a = 2 \quad \therefore (K_{\text{eq}})_2 = \frac{2}{4} = \frac{1}{2}$$

$$\Delta G_1^\circ = -RT_1 \ln(K_{\text{eq}})_1$$

$$\text{Also, } \Delta G_1^\circ = -2RT_2 \ln(K_{\text{eq}})_1 \quad (\text{Given: } T_1 = 2T_2)$$

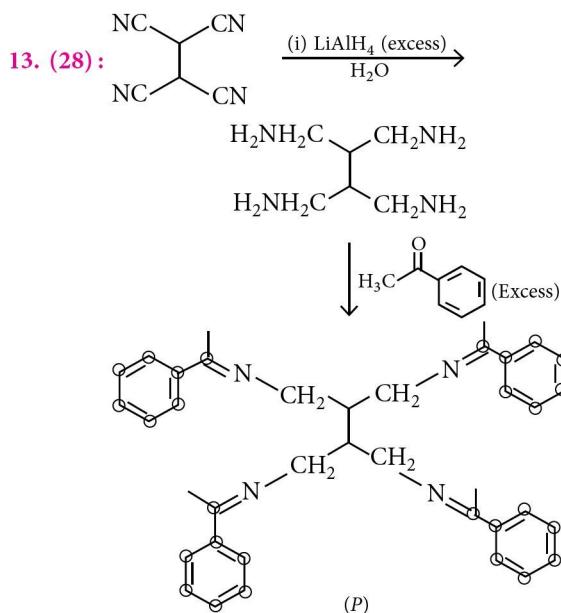
$$\Delta G_2^\circ = -RT_2 \ln(K_{\text{eq}})_2$$

$$\therefore \Delta G_2^\circ - \Delta G_1^\circ = RT_2 \ln \frac{(K_{\text{eq}})_1^2}{(K_{\text{eq}})_2}$$

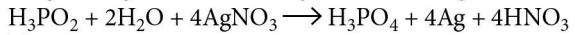
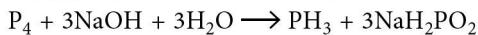
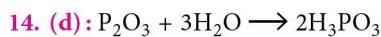
$$= RT_2 \ln \frac{2^2}{1/2} = RT_2 \ln 8$$

$$\text{Hence, } \Delta G^\circ = RT_2 \ln x$$

Thus, the value of x here is 8.

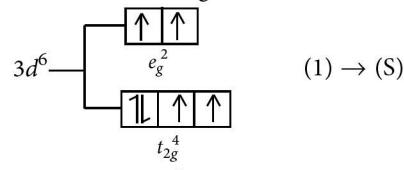


All these circled carbon atoms in product P are sp^2 hybridised.

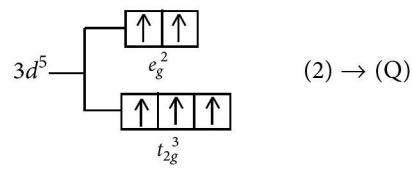


Thus, P \rightarrow 2, Q \rightarrow 3, R \rightarrow 4, S \rightarrow 5

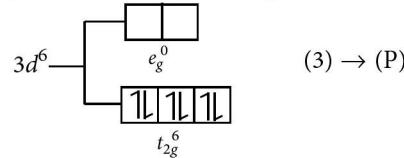
15. (d): (1) In $[Fe(H_2O)_6]^{2+}$, the configuration is $3d^6$. H_2O is a weak field ligand so,



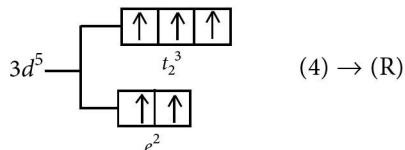
(2) In $[Mn(H_2O)_6]^{2+}$, the configuration is $3d^5$.



(3) In $[Co(NH_3)_6]^{3+}$, the configuration is $3d^6$. NH_3 acts as a strong field ligand therefore,

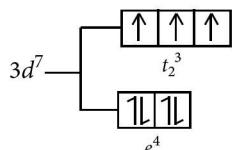


(4) $[\text{FeCl}_4]^- \rightarrow \text{Fe}^{3+}$, the configuration is $3d^5$.
 Cl⁻ is a weak field ligand and does not cause pairing of electrons.

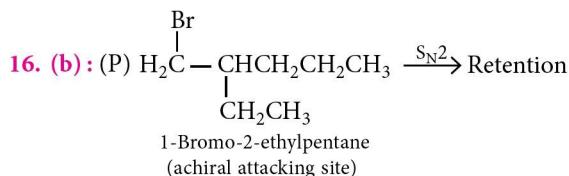


(5) In $[\text{CoCl}_4]^{2-}$, Co²⁺ ion is present.
 $\therefore 3d^7$ configuration.

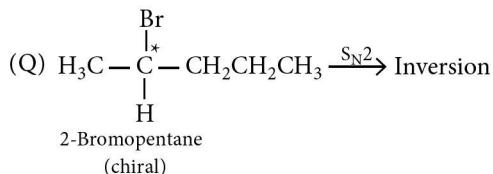
Again, Cl⁻ is a weak field ligand.



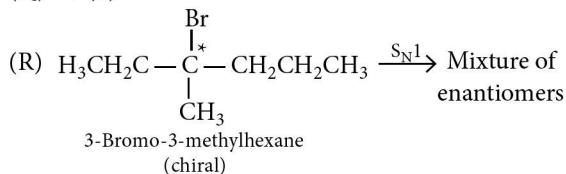
Hence, P \rightarrow 3, Q \rightarrow 2, R \rightarrow 4, S \rightarrow 1



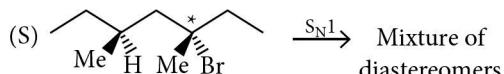
(P) \rightarrow (2)



(Q) \rightarrow (1)



(R) \rightarrow (3)



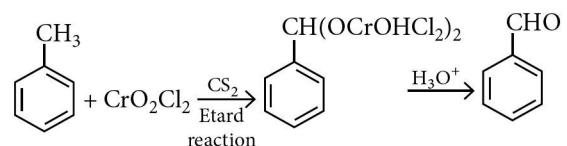
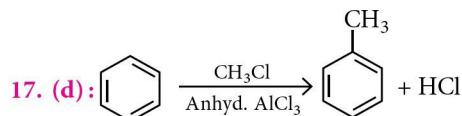
(S) \rightarrow (5)

P is achiral so S_N2 attack will lead to retention of configuration of single enantiomer.

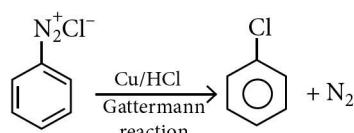
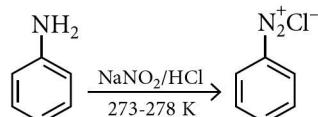
Q is chiral so S_N2 attack will lead to inversion of configuration of single enantiomer.

R is chiral, its S_N1 reaction will give mixture of enantiomers.

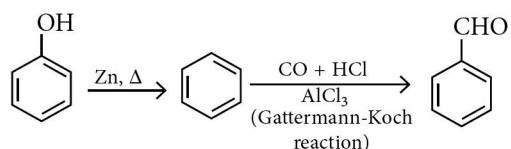
S has two chiral centers having one attacking site. It will give mixture of diastereomers on S_N1 attack.



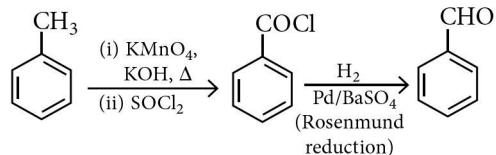
Hence, P \rightarrow 3



Hence, Q \rightarrow 4



Hence, R \rightarrow 5



Hence, S \rightarrow 2

PAPER-II

1. (c): Option (c) represents the correct molecular orbital diagram for F₂ molecule.

2. (a): The formation of micelles takes place only above a particular temperature called Kraft temperature. For Tyndall effect to be observed the refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

Thus, statements I and II are correct.

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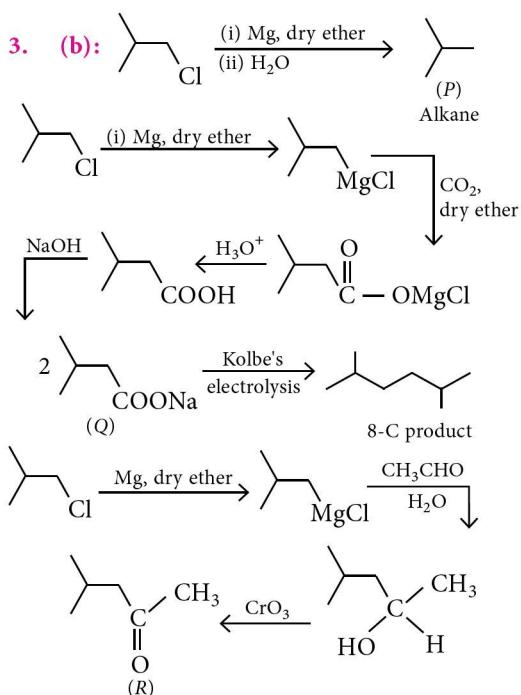
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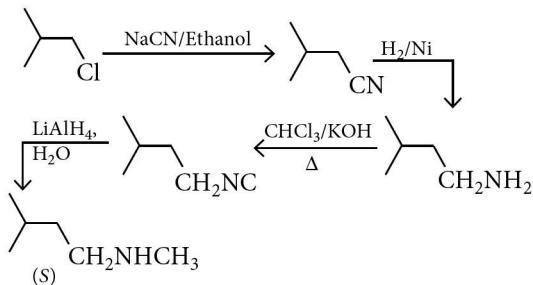
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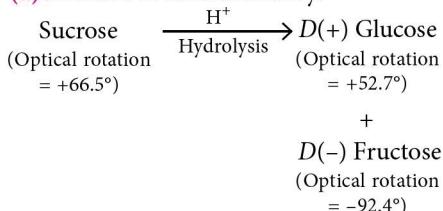


R has α -H atoms. So it cannot undergo Cannizzaro reaction.



S is a secondary amine. Thus option (b) is correct.

4. (a): Sucrose is dextrorotatory.

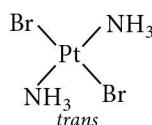
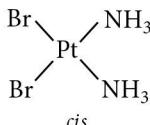


Overall mixture after hydrolysis is

$$\left(\frac{52.7^\circ - 92.4^\circ}{2} = -19.85^\circ \right)$$

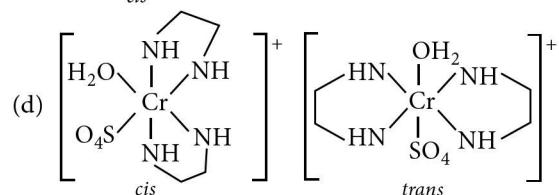
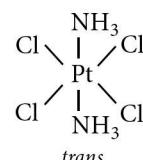
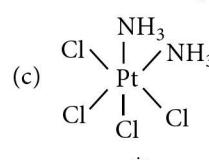
Thus, acid hydrolysis of sucrose (X) leads to leavortatory solution. Sucrose cannot be oxidised by Br₂ water. Hence, (X) is sucrose.

5. (c, d): [Pt(NH₃)₂Br₂] shows geometrical isomerism i.e., cis and trans.



(a) Cis-trans isomerism is not possible in [Pt(en)(SCN)₂].

(b) [Zn(NH₃)₂Cl₂] is tetrahedral, so its cis-trans isomerism is not possible.



6. (a, b, d): Given,

x = Face-centred;	y = Body-centred;	z = Simple-cubic;
Edge length = L_x	Edge length = L_y	Edge length = L_z
Radius = r_x	Radius = r_y	Radius = r_z
Molar mass = M_x	Molar mass = M_y	Molar mass = M_z

Packing efficiency of face-centred > body-centred > simple cubic.

$$\begin{aligned} r_x : r_y : r_z \\ r_x : \frac{8}{\sqrt{3}} r_x : \frac{\sqrt{3}}{2} \times \frac{8}{\sqrt{3}} r_x \\ \therefore r_y > r_z > r_x \end{aligned}$$

$$\begin{aligned} M_x : M_y : M_z \\ M_x : \frac{2}{3} \times 3M_x : 3M_x \\ M_x : 2M_x : 3M_x \\ \therefore M_z > M_y > M_x \end{aligned}$$

$$\begin{aligned} L_x &= \frac{4r_x}{\sqrt{2}} \\ &= 2\sqrt{2}r_x \\ &= 2.83r_x \end{aligned} \quad \begin{aligned} L_y &= \frac{4r_y}{\sqrt{3}} \\ &= \frac{4}{\sqrt{3}} \times \frac{8}{\sqrt{3}} r_x = \frac{32}{3} r_x \\ &= 10.67r_x \end{aligned}$$

$$\therefore L_y > L_z > L_x$$

$$\text{Density, } \rho = \frac{M Z}{N_A L^3}$$

$$\begin{aligned} L_z &= 2r_z \\ &= 2 \times 4 \times r_x \\ &= 8r_x \end{aligned}$$

$$\text{Density of } x, \rho_x = \frac{M_x \times 4}{N_A \times L_x^3} = \frac{M_x \times 4}{N_A \times (2\sqrt{2} r_x)^3}$$

$$= \frac{M_x \times 4}{N_A \times 8 \times 2 \times \sqrt{2} r_x^3} = \frac{M_x}{N_A \times 4\sqrt{2} \times r_x^3}$$

$$\text{Density of } y, \rho_y = \frac{M_y \times 2}{N_A \times L_y^3} = \frac{2M_x \times 2}{N_A \times \left(\frac{32}{3} r_x\right)^3}$$

$$= \frac{2M_x \times 2 \times 27}{N_A \times 32^3 \times r_x^3}$$

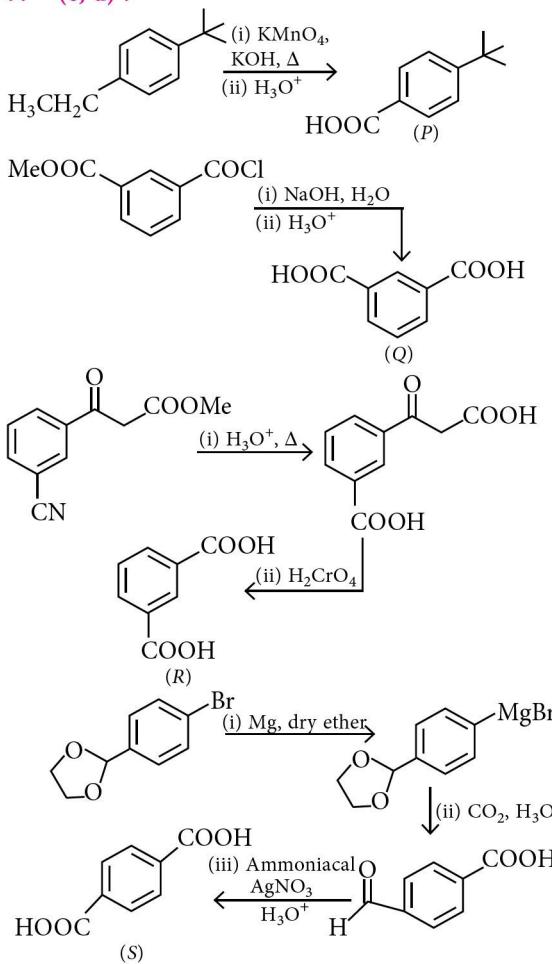
$$\rho_x : \rho_y = \frac{1}{4\sqrt{2}} : \frac{4 \times 27}{32 \times 32 \times 32} = 1 : \frac{4 \times 27 \times 4\sqrt{2}}{32 \times 32 \times 32}$$

$$= 1 : 0.0186$$

Therefore, $\rho_x > \rho_y$

Hence, options (a), (b) and (d) are correct.

7. (c, d) :



(a) Monomers of dacron are ethylene glycol and terephthalic acid. Monomers of glyptal are ethylene glycol and phthalic acid. So, option (a) is incorrect.

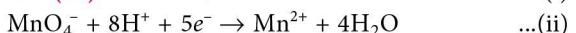
(b) P is not a dicarboxylic acid. So, option (b) is incorrect.

(c) Q and R are same, hence option (c) is correct.

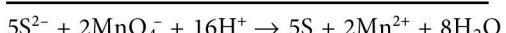
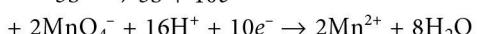
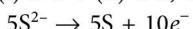
(d) R does not undergo aldol condensation and S does not undergo Cannizzaro reaction.

Hence option (d) is correct.

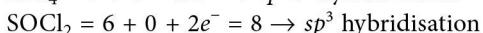
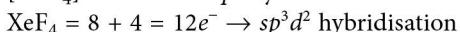
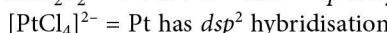
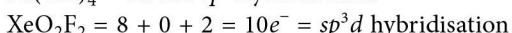
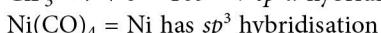
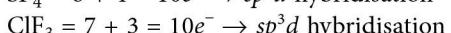
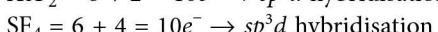
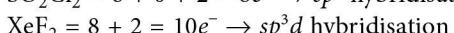
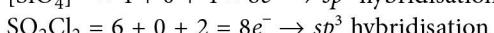
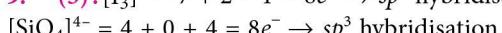
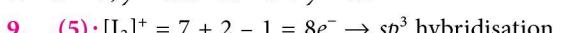
∴ Options (c) and (d) are correct.



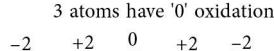
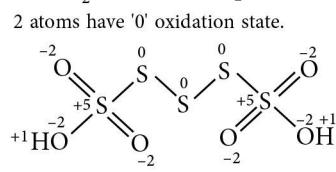
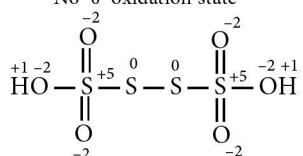
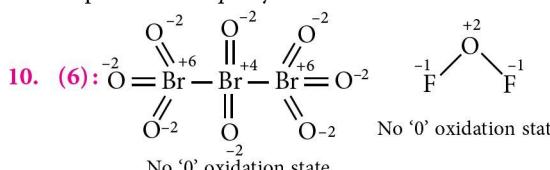
By, (i) $\times 5$ + (ii) $\times 2$, we get



$$\therefore x = 8; y = 10. \therefore x + y = 18$$



∴ 5 species have sp^3 hybridisation.



∴ Total atoms having '0' oxidation state
 $= 2 + 3 + 1 = 6$

$$11. (30.39) : r_n \propto \frac{n^2}{Z}$$

$$r_n = 52.9 \times \frac{n_i^2}{Z}; \quad 26.45 = 52.9 \times \frac{n_f^2}{2}$$

$$105.8 = 52.9 \times \frac{n_i^2}{2}; \quad n_f^2 = \frac{2 \times 26.45}{52.9}$$

$$n_i^2 = \frac{105.8 \times 2}{52.9}; \quad n_f^2 = 1 \Rightarrow n_f = 1$$

$$n_i^2 = 4 \Rightarrow n_i = 2$$

∴ The transition is occurring from $n_i = 2$ to $n_f = 1$

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_H Z^2 \left(1 - \frac{1}{4} \right)$$

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{3}{4} \right)$$

$$\lambda = \frac{4}{3R_H Z^2} = \frac{1}{3R} = \frac{1}{3 \times 109678} \text{ cm}^{-1}$$

[∴ $Z = 2$ for He^+]

$$= 3.039 \times 10^{-6} \text{ cm} = 3.039 \times 10^{-8} \text{ m}$$

$$= 30.39 \text{ nm}$$

12. (682) : 0.2 mole urea is present in 1000 g solvent.

Density of solution = 1.012 g/mL

Mass of 0.2 mole urea = $0.2 \times 60 = 12 \text{ g}$

Mass of solution = $(1000 + 12) \text{ g} = 1012 \text{ g}$

$$\text{Volume of solution} = \frac{1012 \text{ g}}{1.012 \text{ g mL}^{-1}} = 1000 \text{ mL}$$

1000 mL solution contains 0.2 mol urea.

$$50 \text{ mL solution contains} = \frac{0.2 \times 50}{1000} \text{ mol} = 0.01 \text{ mol}$$

In other solution,

$$\text{Number of moles of urea} = \frac{0.06 \text{ g}}{60 \text{ g mol}^{-1}} = 0.001 \text{ mol}$$

$$\therefore \text{Total no. of moles of urea} = (0.01 + 0.001) \\ = 0.011 \text{ mol}$$

Total volume = $50 + 250 = 300 \text{ mL} = 0.3 \text{ L}$

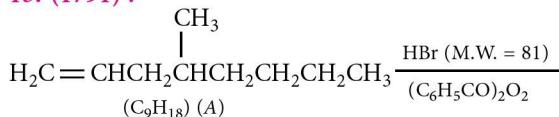
$$\text{Concentration } (c) = \frac{0.011 \text{ mol}}{0.3 \text{ L}}$$

Osmotic pressure, $\pi = cRT$

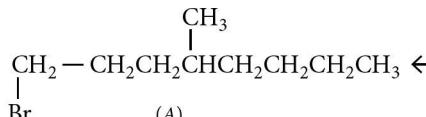
$$= \frac{0.011 \text{ mol}}{0.3 \text{ L}} \times 62 \text{ L Torr K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}$$

$$= 682 \text{ Torr}$$

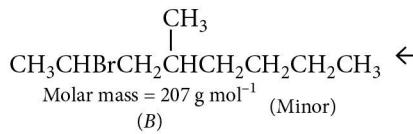
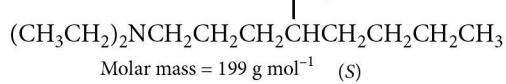
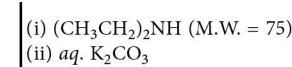
13. (1791) :



Given mass = 2.52 g
 Molar mass = 126 g mol^{-1}
 No. of moles = 0.02



Molar mass = 207 g mol^{-1} (Major)
 Mass = 1.863 g
 No. of moles = 9×10^{-3}



0.02 mol P reacts with 0.02 mol HBr to give 50% of combined products.

No. of mole of combined products = 0.01 mol

Major product (A) is 90%.

$$\therefore \left(0.01 \times \frac{9}{10} \right) \text{ mol} = 9 \times 10^{-3} \text{ mol}$$

1 mol of A gives 1 mol of S

9×10^{-3} mol of A gives 9×10^{-3} mol of S

$$\therefore \text{Mass of S} = 199 \times 9 \times 10^{-3} = 1.791 \text{ g} = 1791 \text{ mg}$$

$$14. (0.31) : \Delta S_{600 \text{ K}} - \Delta S_{300 \text{ K}} = \int_{300}^{600} \frac{1 \times (C_{p,\beta} - C_{p,\alpha}) dT}{T}$$

$$= 1 \times 1 \times \left(\ln \frac{T_2}{T_1} \right)$$

Here, $T_2 = 600 \text{ K}$, $T_1 = 300 \text{ K}$

$$1 - \Delta S_{300 \text{ K}} = 1 \times 1 \times \ln 2$$

$$\Rightarrow \Delta S_{300 \text{ K}} = 1 - 0.69 = 0.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

15. (300) : $\Delta H_{600 \text{ K}} - \Delta H_{300 \text{ K}}$

$$= 1 \times (C_{p,\beta} - C_{p,\alpha})(600 - 300)$$

Now, at transition temperature, i.e., $T_m = 600 \text{ K}$

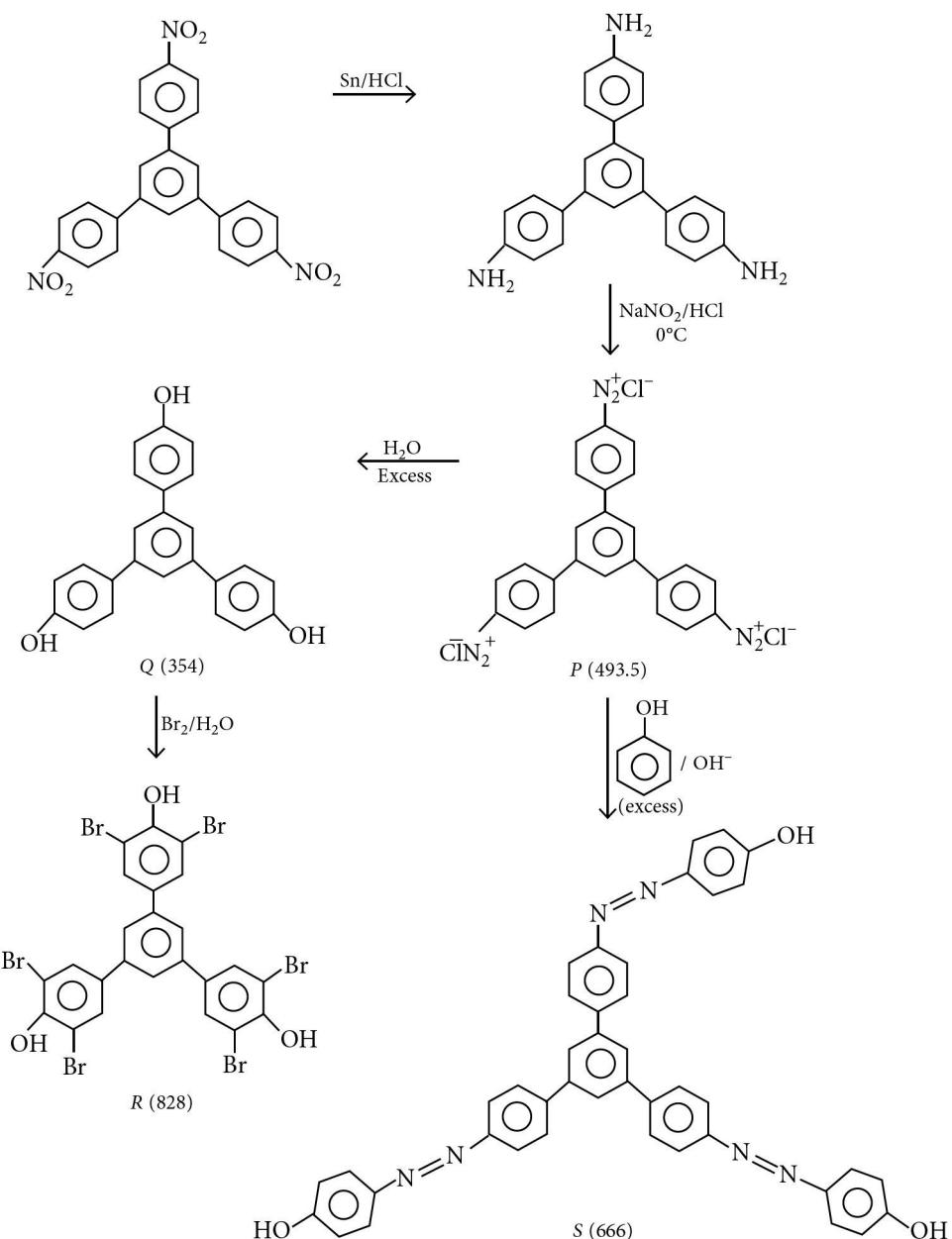
$$\Delta H_{600 \text{ K}} = T_m \Delta S_{600 \text{ K}} = 600 \times (6 - 5)$$

$$= 600 \text{ J mol}^{-1}$$

$$600 - \Delta H_{300 \text{ K}} = 1 \times 1 \times 300$$

$$\Rightarrow \Delta H_{300 \text{ K}} = 600 - 300 = 300 \text{ J mol}^{-1}$$

16. (9) :



M.W. of *R* – M.W. of *Q* = 474 g mol⁻¹
M.W. of *S* – M.W. of *P* = 172.4 g mol⁻¹

No. of heteroatoms in *R* = 9

17. (51) : Total number of C atoms is *S* = 42

Heteroatoms in *S* = 9

Total = 42 + 9 = 51



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SOLVED PAPER 2023

Exam Held
on
6th June

SECTION - A

1. Incorrect set of quantum numbers from the following is
- $n = 4, l = 3, m_l = -3, -2, -1, 0, +1, +2, +3, m_s = -1/2$
 - $n = 5, l = 2, m_l = -2, -1, +1, +2, m_s = +1/2$
 - $n = 4, l = 2, m_l = -2, -1, 0, +1, +2, m_s = -1/2$
 - $n = 5, l = 3, m_l = -3, -2, -1, 0, +1, +2, +3, m_s = +1/2$

2. Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) : Ionisation enthalpy increases along each series of the transition elements from left to right. However, small variations occur.

Reason (R) : There is corresponding increase in nuclear charge which accompanies the filling of electrons in the inner d -orbitals.

In the light of the above statements, choose the most appropriate answer from the options given below :

- (A) is correct but (R) is not correct.
- (A) is not correct but (R) is correct.
- Both (A) and (R) are correct and (R) is the correct explanation of (A).
- Both (A) and (R) are correct but (R) is not the correct explanation of (A).

3. Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) : Lithium and beryllium unlike their other respective group members form compounds with pronounced ionic character.

Reason (R) : Lithium and Magnesium have similar properties due to diagonal relationship.

In the light of the above statements, choose the correct answer from the options given below :

- (A) is true but (R) is false.
- (A) is false but (R) is true.

- (c) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (d) Both (A) and (R) are true but (R) is not the correct explanation of (A).
4. For a weak acid HA, the percentage of dissociation is nearly 1% at equilibrium. If the concentration of acid is 0.1 mol L^{-1} , then the correct option for its K_a at the same temperature is
- 1×10^{-4}
 - 1×10^{-6}
 - 1×10^{-5}
 - 1×10^{-3}
5. The density of 1 M solution of compound 'X' is 1.25 g mL^{-1} . The correct option for the molality of solution is
(Molar mass of compound, X = 85 g mol^{-1})
- 0.705 m
 - 1.208 m
 - 1.165 m
 - 0.858 m
6. Consider the given reaction :
 $\text{CH}_3\text{COCH}_3 \xrightarrow{\text{dil. Ba(OH)}_2} \text{X}$.
- The functional groups present in compound "X" are
- ketone and double bond
 - double bond and aldehyde
 - alcohol and aldehyde
 - alcohol and ketone.
7. The E° value for
 $\text{Al}^+/\text{Al} = +0.55 \text{ V}$ and $\text{Tl}^+/\text{Tl} = -0.34 \text{ V}$
 $\text{Al}^{3+}/\text{Al} = -1.66 \text{ V}$ and $\text{Tl}^{3+}/\text{Tl} = +1.26 \text{ V}$. Identify the incorrect statement.
- Al is more electropositive than Tl.
 - Tl³⁺ is a good reducing agent than Tl⁺.
 - Al⁺ is unstable in solution.
 - Tl can be easily oxidised to Tl⁺ than Tl³⁺.
8. The correct order of dipole moments for molecules NH₃, H₂S, CH₄ and HF, is
- CH₄ > H₂S > NH₃ > HF
 - H₂S > NH₃ > HF > C₄
 - NH₃ > HF > CH₄ > H₂S
 - HF > NH₃ > H₂S > CH₄
9. Molar conductance of an electrolyte increases with dilution according to the equation :

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$$

Which of the following statements are true?

- (A) This equation applies to both strong and weak electrolytes.
 (B) Value of the constant A depends upon the nature of the solvent.
 (C) Value of constant A is same for both BaCl_2 and MgSO_4 .
 (D) Value of constant A is same for both BaCl_2 and Mg(OH)_2 .

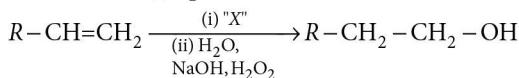
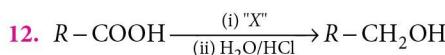
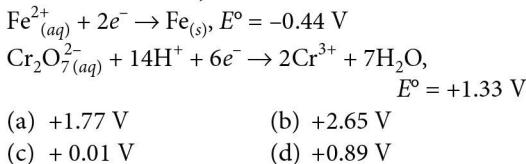
Choose the most appropriate answer from the options given below :

- (a) (A) and (B) only (b) (A), (B) and (C) only
 (c) (B) and (C) only (d) (B) and (D) only

- 10.** Cheilosis occurs due to deficiency of _____.

- (a) thiamine (b) nicotinamide
 (c) pyridoxamine (d) riboflavin

- 11.** The correct value of cell potential in volt for the reaction that occurs when the following two half-cells are connected, is



Identify 'X' in above reactions.

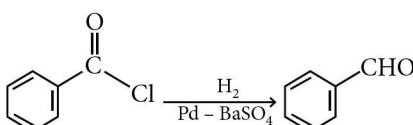
- (a) B_2H_6 (b) LiAlH_4
 (c) NaBH_4 (d) H_2/Pd

- 13.** For a reaction $3A \rightarrow 2B$, the average rate of appearance of B is given by $\frac{\Delta[B]}{\Delta t}$.

The correct relation between the average rate of appearance of B with the average rate of disappearance of A is given in option

- (a) $\frac{-\Delta[A]}{\Delta t}$ (b) $\frac{-3\Delta[A]}{2\Delta t}$ (c) $\frac{-2\Delta[A]}{3\Delta t}$ (d) $\frac{\Delta[A]}{\Delta t}$

- 14.** The following conversion is known as



- (a) Stephen reaction

- (b) Gattermann-Koch reaction

- (c) Etard reaction

- (d) Rosenmund reaction.

- 15.** Which amongst the following is used in controlling depression and hypertension?

- (a) Seldane (b) Valium
 (c) Equanil (d) Prontosil

- 16.** Which one of the following represents all isoelectronic species?

- (a) Na^+ , Cl^- , O^- , NO^+ (b) N_2O , N_2O_4 , NO^+ , NO
 (c) Na^+ , Mg^{2+} , O^- , F^- (d) Ca^{2+} , Ar , K^+ , Cl^-

- 17.** Given below are two statements :

Statement I: The value of wave function, ψ depends upon the coordinates of the electron in the atom.

Statement II : The probability of finding an electron at a point within an atom is proportional to the orbital wave function.

In the light of the above statements, choose the correct answer from the options given below :

- (a) Statement I is true but Statement II is false.
 (b) Statement I is false but Statement II is true.
 (c) Both Statement I and Statement II are true.
 (d) Both Statement I and Statement II are false.



ANSWERS JUNE 2023

The 3 sets of trio are (**TAL, ALT, LAT**), (**ULT, LUT, TUL**), (**MAG, GAM, AGM**)

CATALYST

MALTOSE

LATEX

PENULTIMATE

LUTETIUM

SPATULA

MAGNALIUM

AMALGAM

FRAGMENTATION

Winners : Kaushikumar Kevadiya,
 Ujjwal Kumar, Sourish Dhara, Sujatha Shetty

18. The correct van der Waals equation for 1 mole of a real gas is

- (a) $\left(p + \frac{a}{V^2} \right) (V - b) = RT$
- (b) $\left(p + \frac{V^2}{a} \right) (V - b) = RT$
- (c) $\left(p + \frac{an^2}{V^2} \right) (V^2 - nb) = RT$
- (d) $\left(p + \frac{an^2}{V^2} \right) (V - nb) = nRT$

19. The correct option in which the density of argon (Atomic mass = 40) is highest

- (a) STP (b) 0°C, 2 atm
- (c) 0°C, 4 atm (d) 273°C, 4 atm

20. Which of the following is correctly matched?

- (a) Basic oxides \Rightarrow In₂O₃, K₂O, SnO₂
- (b) Neutral oxides \Rightarrow CO, NO₂, N₂O
- (c) Acidic oxides \Rightarrow Mn₂O₇, SO₂, TeO₃
- (d) Amphoteric oxides \Rightarrow BeO, Ga₂O₃, GeO

21. Which of the following is a positively charged sol?

- (a) Methylene blue sol (b) Congo red sol
- (c) Silver sol (d) Sb₂S₃ sol

22. Match List-I with List-II.

List-I (Mixtures/Sample)		List-II (Technique used for purification)	
(A)	Glycerol from spent lye	(I)	Steam distillation
(B)	Chloroform + Aniline	(II)	Fractional distillation
(C)	Fractions of crude oil	(III)	Distillation under reduced pressure
(D)	Aniline + Water	(IV)	Distillation

Choose the correct answer from the options given below :

- (a) (A) - (III), (B) - (IV), (C) - (II), (D) - (I)
- (b) (A) - (IV), (B) - (II), (C) - (I), (D) - (III)
- (c) (A) - (I), (B) - (II), (C) - (III), (D) - (IV)
- (d) (A) - (I), (B) - (III), (C) - (II), (D) - (IV)

23. Which amongst the following reactions of alkyl halides produces isonitrile as a major product?

- (A) $R - X + HCN \rightarrow$
- (B) $R - X + AgCN \rightarrow$
- (C) $R - X + KCN \rightarrow$
- (D) $R - X + NaCN \xrightarrow[C_2H_5OH]{H_2O}$

Choose the most appropriate answer from the options given below :

- (a) (D) only (b) (C) and (D) only
- (c) (B) only (d) (A) and (B) only

24. Match List-I with List-II.

List-I (Hydride)		List-II (Type of hydride)	
(A)	NaH	(I)	Electron precise
(B)	PH ₃	(II)	Saline
(C)	GeH ₄	(III)	Metallic
(D)	LaH _{2.87}	(IV)	Electron rich

Choose the correct answer from the options given below:

- (a) (A) - (III), (B) - (IV), (C) - (II), (D) - (I)
- (b) (A) - (II), (B) - (III), (C) - (IV), (D) - (I)
- (c) (A) - (I), (B) - (III), (C) - (II), (D) - (IV)
- (d) (A) - (II), (B) - (IV), (C) - (I), (D) - (III)

25. Which one of the following statements is incorrect related to Molecular Orbital Theory?

- (a) The π^* anti-bonding molecular orbital has a node between the nuclei.
- (b) In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other.
- (c) Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are symmetrical around the bond axis.
- (d) A π -bonding molecular orbital has larger electron density above and below the internuclear axis.

26. An acidic buffer is prepared by mixing

- (a) weak acid and its salt with strong base.
- (b) equal volumes of equimolar solutions of weak acid and weak base.
- (c) strong acid and its salt with strong base.
- (d) strong acid and its salt with weak base.

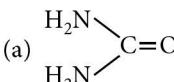
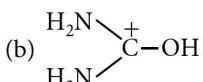
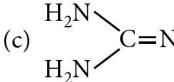
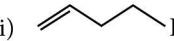
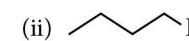
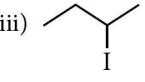
(The pK_a of acid = pK_b of the base)

27. Reagents which can be used to convert alcohols to carboxylic acids, are :

- (A) CrO₃ - H₂SO₄ (B) K₂Cr₂O₇ + H₂SO₄
- (C) KMnO₄ + KOH/H₃O⁺ (D) Cu, 573 K
- (E) CrO₃, (CH₃CO)₂O

Choose the most appropriate answer from the options given below :

- (a) (B), (C) and (D) only
- (b) (B), (D) and (E) only
- (c) (A), (B) and (C) only
- (d) (A), (B) and (E) only

- 28.** Select the element (*M*) whose trihalides cannot be hydrolysed to produce an ion of the form $[M(H_2O)_6]^{3+}$.
- (a) Ga (b) In (c) Al (d) B
- 29.** The correct option for the rate law that corresponds to overall first order reaction is
- (a) Rate = $k [A]^0 [B]^2$ (b) Rate = $k [A] [B]$
 (c) Rate = $k [A]^{1/2} [B]^2$ (d) Rate = $k [A]^{-1/2} [B]^{3/2}$
- 30.** Which amongst the following compounds/species is least basic?
- (a)  (b) 
 (c)  (d) 
- 31.** Which of the following forms a set of a complex and a double salt, respectively?
- (a) $CuSO_4 \cdot 5H_2O$ and $CuCl_2 \cdot 4NH_3$
 (b) $PtCl_2 \cdot 2NH_3$ and $PtCl_4 \cdot 2HCl$
 (c) $K_2PtCl_2 \cdot 2NH_3$ and $KAl(SO_4)_2 \cdot 12H_2O$
 (d) $NiCl_2 \cdot 6H_2O$ and $NiCl_2(H_2O)_4$
- 32.** Given below are two statements :
- Statement I :** High density polythene is formed in the presence of catalyst triethylaluminium and titanium tetrachloride.
- Statement II :** High density polymers are chemically inert.
- In the light of the above statements, choose the correct answer from the options given below :
- (a) Statement I is correct but Statement II is false.
 (b) Statement I is incorrect but Statement II is true.
 (c) Both Statement I and Statement II are true.
 (d) Both Statement I and Statement II are false.
- 33.** Which amongst the following compounds will show geometrical isomerism?
- (a) Pent-1-ene
 (b) 2,3-Dimethylbut-2-ene
 (c) 2-Methylprop-1-ene
 (d) 3,4-Dimethylhex-3-ene
- 34.** Given below are two statements :
- Statement I :** Hydrated chlorides and bromides of Ca, Sr and Ba on heating undergo hydrolysis.
- Statement II :** Hydrated chlorides and bromides of Be and Mg on heating undergo dehydration.
- In the light of the above statements, choose the correct answer from the options given below :
- (a) Statement I is correct but Statement II is false.
 (b) Statement I is incorrect but Statement II is true.
 (c) Both Statement I and Statement II are true.
 (d) Both Statement I and Statement II are false.
- 35.** The correct order for the rate of α , β -dehydrohalogenation for the following compounds is _____.
- (i)  (ii) 
 (iii) 
- (a) (i) < (ii) < (iii) (b) (ii) < (i) < (iii)
 (c) (iii) < (ii) < (i) (d) (ii) < (iii) < (i)

SECTION - B

Attempt any 10 questions out of 15.

- 36.** How many number of tetrahedral voids are formed in 5 mol of a compound having cubic close packed structure? (Choose the correct option.)
- (a) 1.550×10^{24} (b) 3.011×10^{25}
 (c) 3.011×10^{24} (d) 6.022×10^{24}
- 37.** Type of isomerism exhibited by compounds $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2H_2O$, $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ and the value of coordination number (CN) of central metal ion in all these compounds, respectively is
- (a) geometrical isomerism, CN = 2
 (b) optical isomerism, CN = 4
 (c) ionisation isomerism, CN = 4
 (d) solvate isomerism, CN = 6.
- 38.** The correct sequence given below containing neutral, acidic, basic and amphoteric oxide each, respectively, is
- (a) NO, ZnO, CO_2 , CaO (b) ZnO, NO, CaO, CO_2
 (c) NO, CO_2 , ZnO, CaO (d) NO, CO_2 , CaO, ZnO

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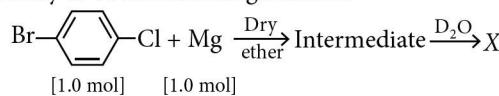
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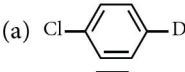
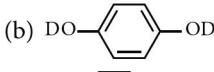
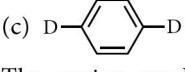
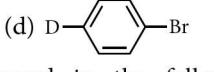
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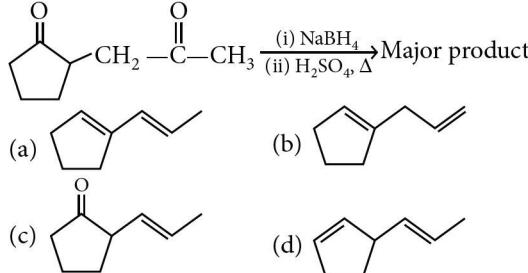
- 39.** Read the following statements and choose the set of correct statements :
- Chrome steel is used for cutting tools and crushing machines.
 - The fine dust of aluminium is used in paints and lacquers.
 - Copper is used for reduction of alcohol.
 - Zinc dust is used as a reducing agent in the manufacture of paints.
 - Iron is used for galvanising zinc.
- Choose the most appropriate answer from the options given below :
- (D) and (E) only
 - (A) and (D) only
 - (A), (B) and (D) only
 - (B), (C) and (D) only
- 40.** Choose the correct sequence of reagents in the conversion of 4-nitrotoluene to 2-bromotoluene.
- NaNO_2/HCl ; Sn/HCl ; Br_2 ; $\text{H}_2\text{O}/\text{H}_3\text{PO}_2$
 - Sn/HCl ; NaNO_2/HCl ; Br_2 ; $\text{H}_2\text{O}/\text{H}_3\text{PO}_2$
 - Br_2 ; Sn/HCl ; NaNO_2/HCl ; $\text{H}_2\text{O}/\text{H}_3\text{PO}_2$
 - Sn/HCl ; Br_2 ; NaNO_2/HCl ; $\text{H}_2\text{O}/\text{H}_3\text{PO}_2$
- 41.** How are edge length ' a ' of the unit cell and radius ' r ' of the sphere related to each other in *ccp* structure? (Choose correct option for your answer.)
- $a = 2r$
 - $a = r/2\sqrt{2}$
 - $a = 4r/\sqrt{3}$
 - $a = 2\sqrt{2}r$
- 42.** Identify the product in the following reaction.
- (i) KCN
 (ii) $\text{H}_2\text{O}/\text{HCl}, \Delta$
 (iii) $\text{Br}_2/\text{red phosphorus}$
 (iv) H_2O
- Product
- (a)
- (b)
- (c)
- (d)
- 43.** Given below are two statements :
- Statement I :** In an organic compound, when inductive and electromeric effects operate in opposite directions, the inductive effect predominates.
- Statement II :** Hyperconjugation is observed in *o*-xylene.
- In the light of the above statements, choose the correct answer from the options given below :
- Statement I is true but Statement II is false.
 - Statement I is false but Statement II is true.
- 44.** The correct option for a redox couple is
- both are oxidised forms involving same element
 - both are reduced forms involving same element
 - both the reduced and oxidized forms involve same element
 - cathode and anode together.
- 45.** Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).
- Assertion (A) :** Ionisation enthalpies of early actinoids are lower than for early lanthanoids.
- Reason (R) :** Electrons are entering $5f$ orbitals in actinoids which experience greater shielding from nuclear charge.
- In the light of the above statements, choose the correct answer from the option given below :
- (A) is true but (R) is false.
 - (A) is false but (R) is true.
 - Both (A) and (R) are true and (R) is the correct explanation of (A).
 - Both (A) and (R) are true but (R) is not the correct explanation of (A).
- 46.** Consider the following reaction :
- $$2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)}; \Delta_r H^\circ = -483.64 \text{ kJ}$$
- What is the enthalpy change for decomposition of one mole of water ? (Choose the right option.)
- 120.9 kJ
 - 241.82 kJ
 - 18 kJ
 - 100 kJ
- 47.** Which statement is not true about photochemical smog?
- Photochemical smog is harmful to humans but has no effect on plants.
 - Plants like Pinus, Juniperus can help in reducing the photochemical smog.
 - Photochemical smog occurs in warm, dry and sunny climate.
 - Common components of photochemical smog are ozone, nitric oxide, acrolein, formaldehyde and peroxyacetyl nitrate.
- 48.** Which amongst the following aqueous solutions of electrolytes will have minimum elevation in boiling point? (Choose the correct option.)
- 0.05 M NaCl
 - 0.1 M KCl
 - 0.1 M MgSO_4
 - 1 M NaCl

49. Identify 'X' in the following reaction.



- (a)  (b) 
- (c)  (d) 

50. The major product formed in the following conversion is _____.



SOLUTIONS

1. (b) : For a given value of l , m_l has $(2l + 1)$ values. For $l = 2$, the number of m_l values is $[2(2)+1] = 5$. But in set (b), only four values of m_l are given. The values of m_l range from $-l$ to $+l$ including 0.

Hence, the possible m_l values for the given orbital are $-2, -1, 0, +1, +2$.

2. (c) : Due to corresponding increase in nuclear charge which accompanies the filling of the inner d -orbitals, there is an increase in ionisation enthalpy along each series of the transition elements from left to right. Although, many small variations occur.

3. (b) : Li and Be forms predominantly covalent compounds due to small charge and high charge density. The similarity in properties between lithium and magnesium arises due to diagonal relationship.

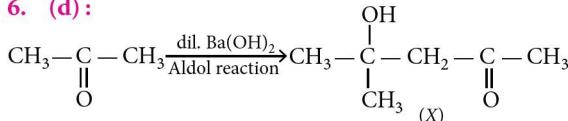
4. (c) : $K_a = C\alpha^2$
 $K_a = (0.1) \times (0.01)^2 = 1 \times 10^{-5}$

5. (d) : $m = \frac{1000 \times M}{1000 \times d - (MM_w)}$

Here, M = molarity of the solution, d = density of solution, MM_w = Molar mass of the solute

$$m = \frac{1000 \times 1}{(1000 \times 1.25) - (1 \times 85)} = \frac{1000}{1165} = 0.858 \text{ m}$$

6. (d) :



Thus, functional groups present in product 'X' are alcohol and ketone.

7. (b) : Ti^{3+} acts as an oxidising agent and not reducing agent.

8. (d) : A given molecule possesses dipole moment as a result of polarisation. Polarisation arises in a hetero nuclear molecule due to significant electronegativity difference between atoms involved in covalent bond formation. The shared electron pair gets displaced towards more electronegative atom and the resultant covalent bond is polar covalent bond.

Thus, the correct order is : $\text{HF} > \text{NH}_3 > \text{H}_2\text{S} > \text{CH}_4$
 (Non-polar)

9. (d) : The given equation is applicable only to strong electrolytes. For strong electrolytes, Λ_m increases slowly with dilution and is thus, represented by the given equation. The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte, i.e., the charge on the cation and anion produced on the dissociation of the electrolyte in the solution. Value of constant 'A' is same for both BaCl_2 and $\text{Mg}(\text{OH})_2$.

10. (d) : Cheilosis (Fissuring at corners of mouth and lips) occurs due to deficiency of vitamin B_2 (Riboflavin).

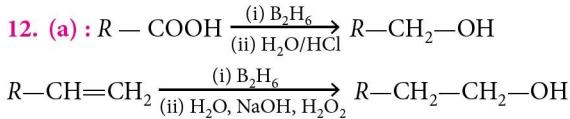
11. (a) : $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$
 $= (+1.33) - (-0.44) = +1.77 \text{ V}$



Here are the nine shuffled words containing 3 sets of trio. The three letters of trio can be arranged in any sequence. Complete these words by finding 3 sets of trio.

F — — SPAR
 E — — ER
 M — — L
 A — — HYDE
 A — — CILLIN
 P — — —
 SE — — ERMEABLE
 BENZO — —
 — — — IQUESCENT

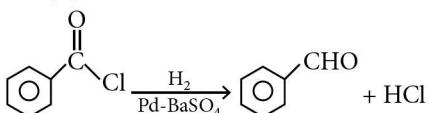
Readers can send their responses at editor@mtg.in or post us with complete address by 10th of every month.
 Winners' names will be published in next issue.



13. (c) : $3A \rightarrow 2B$

$$r = -\frac{1}{3} \frac{\Delta [A]}{\Delta t} = +\frac{1}{2} \frac{\Delta [B]}{\Delta t} \Rightarrow \frac{\Delta [B]}{\Delta t} = -\frac{2}{3} \frac{\Delta [A]}{\Delta t}$$

14. (d) : Rosenmund reaction :



15. (c) : Equanil is a tranquilizer that is used in controlling depression and hypertension.

16. (d) : Total numbers electrons are same in all the species as follows :



17. (a) : The square of the wave function (ψ^2) at a point gives the probability density of the electron at that point.

18. (a) : The van der Waals equation for 1 mole of a real gas is : $\left(p + \frac{a}{V^2} \right) (V - b) = RT$

19. (c) : $\rho = \frac{PM}{RT}$. For maximum density, pressure (P) should be maximum and temperature (T) should be minimum.

20. (c) : $\text{Mn}_2\text{O}_7, \text{SO}_2$ and TeO_3 are acidic oxides.

21. (a) : Methylene blue sol is a positively charged sol.

22. (a) : (A) Glycerol from spent lye \rightarrow Distillation under reduced pressure

(B) Chloroform + Aniline \rightarrow Distillation

(C) Fractions of crude oil \rightarrow Fractional distillation

(D) Aniline + Water \rightarrow Steam distillation

23. (c) : In A, C and D, nitrile is formed as the major product.

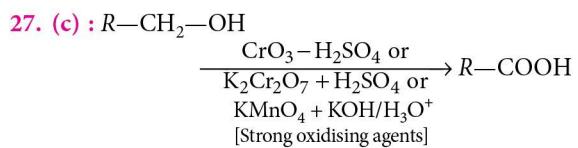


Alkyl isocyanide (or isonitrile)

24. (d)

25. (c) : Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis.

26. (a) : Acidic buffer is prepared by mixing weak acid and its salt with a strong base.



28. (d) : Maximum covalency of boron is four due to the absence of d -orbitals. Hence, its trihalide cannot be hydrolysed to produce an ion of the form $[\text{M}(\text{H}_2\text{O})_6]^{3+}$.

29. (d) : $r = k[A]^{-1/2} [B]^{3/2}$

$$\text{Order} = -\frac{1}{2} + \frac{3}{2} = 1$$

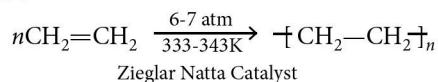
30. (b)

31. (c) : A complex salt is defined as a compound composed of a central metal atom having coordination bonds with ligands around it. While, double salts are defined as the ionic compounds that are formed by the combination of two different salt compounds.

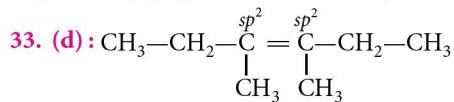
Complex salt is $\text{K}_2[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Double salt is $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (potash alum).

32. (c) : High density polythene is formed from ethene in the presence of Ziegler Natta catalyst (triethylaluminium and titanium tetrachloride) as follows :



High density polymers are chemically inert.

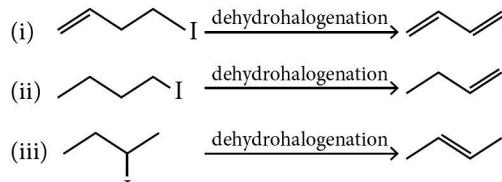


3,4-Dimethylhex-3-ene

It shows geometrical isomerism.

34. (d) : Hydrated chlorides and bromides of Ca, Sr and Ba are ionic, thus they undergo dehydration after heating. Hydrated chlorides and bromides of Be and Mg are covalent thus they undergo hydrolysis on heating.

35. (d) :



Rate of dehydrohalogenation of the alkyl halides depends on the stability of the alkene formed. Alkene formed in case (i) is most stable (conjugated diene), followed by (iii), which is a more substituted alkene.

The alkene formed in case (ii) is least stable as it is least substituted.
 \therefore Rate of dehydrohalogenation : (ii) < (iii) < (i)

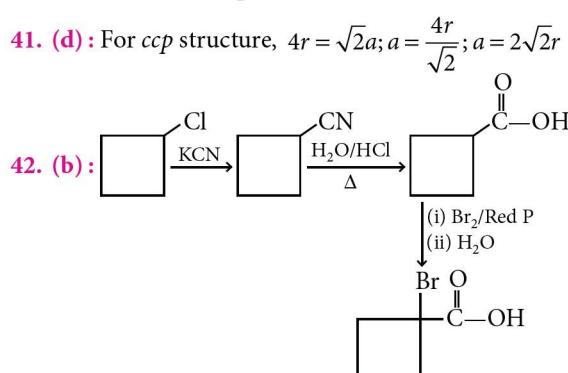
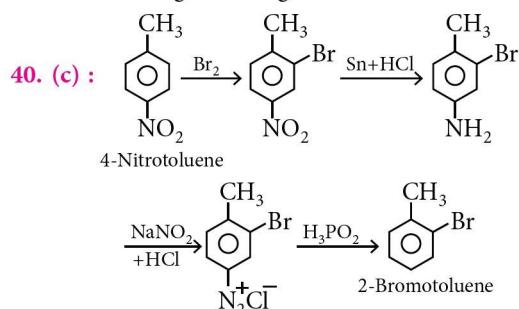
36. (d): Number of particles in a compound = $5N_A$
 Number of tetrahedral voids = $2 \times$ number of particles
 (for close packed structure)
 $= 2 \times 5N_A = 10N_A = 10 \times 6.022 \times 10^{23} = 6.022 \times 10^{24}$

37. (d): The isomers that exhibit solvate isomerism have the same composition but differ with respect to the number of solvent ligand molecules as well as the counter ion in the crystal lattice.

Given complex compounds exhibit solvate isomerism and the coordination number of central metal ion is 6.

38. (d)

39. (c) : Copper is used for oxidation of alcohol.
 Zinc is used for galvanising iron.

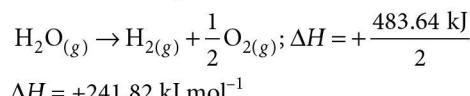


43. (b)

44. (c) : Redox couple is both the reduced and oxidised forms involving same element.

45. (c) : Early actinoids have low ionisation enthalpy than early lanthanoids because $5f$ electrons have more effective shielding from nuclear charge than $4f$ electrons.

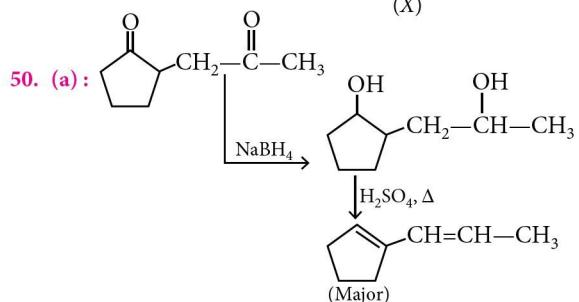
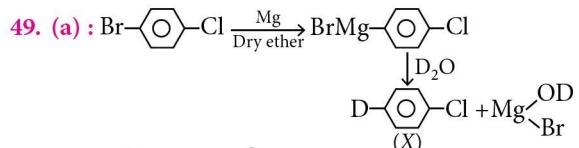
46. (b) : Decomposition for 1 mole of water,



47. (a)

48. (a) : $i \times M \downarrow \Rightarrow \Delta T_b \downarrow$

Electrolyte	$i \times M$
NaCl	$2 \times 0.05 = 0.1$
KCl	$2 \times 0.1 = 0.2$
MgSO ₄	$2 \times 0.1 = 0.2$
NaCl	$2 \times 1 = 2$



Winners : Kaushikkumar Kevadiya , Sujatha Shetty

SOLUTIONS TO JUNE 2023 WORD GRID

T	X	O	P	Q	P	Q	R	A	B	E	D	H	I	J	Z
S	Y	E	X	S	T	N	M	S	T	O	C	G	P	U	P
Z	[E]	L	E	C	T	R	O	D	I	A	L	Y	S	I	S
A	V	W	R	R	B	S	T	U	V	P	O	C	Z	X	T
N	T	O	S	Q	R	G	Z	Y	L	K	N	I	U	V	W
B	U	T	A	N	N	N	B	N	M	R	P	T	N	U	
C	S	V	M	S	N	Q	I	T	D	C	O	T	I	V	P
O	R	W	A	T	Z	S	E	O	O	O	Z	S	N	W	O
P	Q	P	L	P	E	T	F	N	S	R	Y	T	N	X	N
Q	X	B	G	O	A	P	I	B	C	W	X	S	I	Y	Z
T	R	S	A	N	O	S	D	O	T	U	V	T	N	Q	G
N	A	O	M	W	A	G	W	E	F	S	W	S	G	R	H
B	V	P	N	T	N	D	Q	A	F	D	X	U	Z	W	W
O	C	T	I	V	P	C	T	R	C	T	S	V	E	X	A
S	T	O	I	R	S	O	B	S	U	K	T	R	Y	O	
S	N	T	S	U	B	S	T	R	A	T	E	R	S	Z	N
Q	R	U	S	O	P	Q	W	E	F	G	I	R	O	N	R
V	W	[C]	R	A	C	K	I	N	G	J	K	L	L	M	T

1. Amalgam
2. Electrodialysis
3. Zircon
4. Wacker
5. Bronze
6. Cracking
7. Tinning
8. Substrate

WORD GRID



Readers are
requested to send
their responses of
word grid.
Be the Winner!

Find and encircle the words in the given grid, running in one of the possible directions; horizontal, vertical or diagonal by reading the clues given below.

S	Y	E	X	S	T	N	M	F	U	M	E	S	P	U	P	
Z	E	L	E	C	T	G	U	A	I	O	L	Y	I	I	S	
A	V	W	R	R	B	S	T	U	V	P	O	C	N	X	T	
N	T	O	S	N	R	P	W	Y	S	K	N	I	F	U	W	
B	U	T	A	O	O	H	A	B	A	M	R	P	U	N	U	
C	S	V	M	D	N	O	T	T	C	C	O	T	S	V	P	
O	R	W	A	E	Z	S	C	Q	C	O	Z	S	I	W	O	
P	Q	P	L	P	E	P	H	N	H	R	Y	T	O	X	N	
Q	X	B	G	O	A	H	L	B	A	W	X	S	N	Y	Z	
T	R	S	A	N	O	A	U	O	R	U	V	T	N	Q	G	
N	A	O	M	W	W	A	T	V	E	I	S	W	S	G	R	H
B	V	P	N	T	N	A	O	A	N	D	X	U	Z	W	W	
O	C	T	I	V	P	S	S	R	A	T	S	V	E	X	A	
S	T	O	I	P	A	E	K	O	R	W	Q	X	G	U	O	
S	N	T	S	M	I	S	C	I	B	I	L	I	T	Y	N	
M	I	C	R	O	B	A	L	A	N	C	E	K	O	N	R	

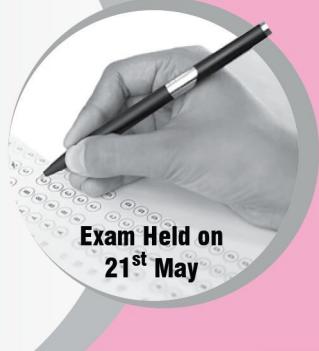
Clues

1. A location in an orbital, where the probability of finding an electron is zero.
2. It is the property of two substances to mix in all proportions, forming a homogeneous mixture.
3. These are a type of non-viable particulates that are obtained by condensation of vapours during boiling, distillation or other chemical processes.
4. A group of enzymes that use water to cleave a phosphoric acid monoester into a phosphate ion and an alcohol.
5. It is a crystalline sesquiterpenoid alcohol found especially in the oil of guaiacum wood.
6. A dilute solution containing the water soluble components of vegetable drugs prepared by aqueous extraction of the drugs.
7. A balance capable of detecting and measuring changes in weight of the order of 10^{-6} g.
8. It is an artificial sweetening agent that is 550 times sweeter than sugar.



*Please send entries of solutions both with words and scanned copy of the grid by 10th of every month.

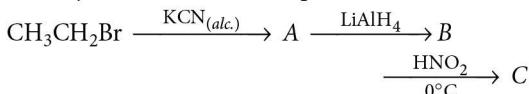
SOLVED PAPER 2023



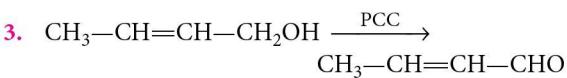
Karnataka CET

(MULTIPLE CHOICE QUESTIONS)

1. A pair of compounds having the same boiling points are
 - (a) *cis* but-2-ene and *trans* but-2-ene
 - (b) *n*-hexane and *neo*-hexane
 - (c) benzene and naphthalene
 - (d) (+) butan-2-ol and (-) butan-2-ol.
 2. Identify A, B and C in the sequence :



- (a) $\text{CH}_3\text{CH}_2\text{CN}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 (b) $\text{CH}_3\text{CH}_2\text{NC}$, $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
 (c) $\text{CH}_3\text{CH}_2\text{CN}$, $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{N}_2\text{Cl}$
 (d) $\text{CH}_3\text{CH}_2\text{CN}$, $\text{CH}_3\text{CH}_2\text{NH}_2$, $\text{C}_2\text{H}_5\text{OH}$



Hybridisation change involved at C-1 in the above reaction is

en : Ni :: 1 : 1, 2 : 1, 3 : 1 to $[Ni(H_2O)_6]^{2+}$ aq. solution, following co-ordination entities are formed.

- I. $[\text{Ni}(\text{H}_2\text{O})_4\text{en}]^{2+}_{(aq)}$ - pale blue
 II. $[\text{Ni}(\text{H}_2\text{O})_5(\text{en})]^{2+}$ - blue/purple

III. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ - violet

- The wavelength in nm of light absorbed

The wavelength in nm of light absorbed in case of I and III are respectively

- I and III are respectively
(a) 475 nm and 310 nm

(b) 300 nm and 475 nm

- (c) 310 nm and 500 nm

(d) 600 nm and 535 nm

- (d) 600 nm and 535 nm

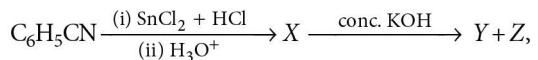
5. Which of the following is an organometallic compound?

 - (a) CH_3COONa
 - (b) $\text{CH}_3\text{CH}_2\text{MgBr}$
 - (c) $(\text{CH}_3\text{COO})_2\text{Ca}$
 - (d) CH_3ONa

6. A better reagent to oxidize primary alcohols into aldehyde is

 - (a) PCC
 - (b) alkaline KMnO_4
 - (c) acidified $\text{K}_2\text{Cr}_2\text{O}_7$
 - (d) CrO_3 .

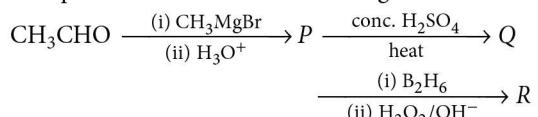
7. In the reaction :



Formation of X, formation of Y and Z are known by

- (a) Rosenmund reduction, Cannizzaro reaction
 - (b) Clemmensen reduction, Sandmeyer reaction
 - (c) Wolff-Kishner reduction, Wurtz reaction
 - (d) Stephen reaction, Cannizzaro reaction.

8. Compounds *P* and *R* in the following reaction are :



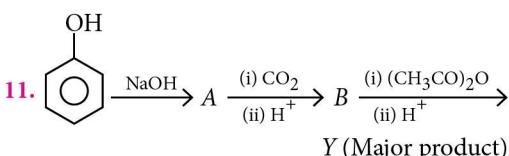
- (a) position isomers (b) functional isomers
(c) metamers (d) identical

- 9.** Aniline does not undergo

- (a) nitration
 - (b) sulphonation
 - (c) Friedel – Crafts reaction
 - (d) bromination.

10. The heating of phenyl methyl ether with HI produces an aromatic compound A which on treatment with conc. HNO_3 gives B. A and B respectively are,

 - (a) methanol, ethanoic acid
 - (b) picric acid, phenol
 - (c) iodobenzene, 1-iodo-4-nitrobenzene
 - (d) phenol, picric acid.



Y in the above reaction is

- (a) salicylaldehyde
- (b) aspirin
- (c) cumene
- (d) picric acid.

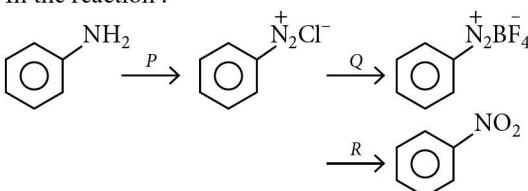
12. Sucrose is dextrorotatory but after hydrolysis the mixture shows laevorotation, this is because of
 (a) laevorotation of glucose is more than dextrorotation of fructose
 (b) sucrose is a non-reducing sugar
 (c) racemic mixture is formed
 (d) laevorotation of fructose is more than dextrorotation of glucose.

13. The correct order of match between column X and column Y is

X		Y	
I.	Vitamin A	(i)	Muscular weakness
II.	Vitamin D	(ii)	Increased blood clotting time
III.	Vitamin E	(iii)	Night-blindness
IV.	Vitamin K	(iv)	Osteomalacia

- (a) I-(iv), II-(iii), III-(ii), IV-(i)
- (b) I-(ii), II-(i), III-(iii), IV-(iv)
- (c) I-(iii), II-(ii), III-(iv), IV-(i)
- (d) I-(iii), II-(iv), III-(i), IV-(ii)

14. In the reaction :



P, Q and R respectively are

- (a) $\text{NaNO}_2 + \text{dil. HCl}, \text{HBF}_4, \text{Cu} + \text{NaNO}_2$
- (b) $\text{NaNO}_2 + \text{conc. HCl}, \text{F}_2, \text{Cu} + \text{NaNO}_3$
- (c) $\text{NaNO}_2 + \text{dil. HCl}, \text{BF}_3, \text{Cu} + \text{NaNO}_2$
- (d) $\text{NaNO}_3 + \text{dil. HCl}, \text{F}_2, \text{Cu} + \text{NaNO}_3$

15. Thyroxine produced in the thyroid gland is an iodinated derivative of _____ .

- (a) threonine
- (b) lysine
- (c) tyrosine
- (d) tryptophan

16. Which one of the following is a non-narcotic analgesic?

- (a) Heroin
- (b) Codeine
- (c) Aspirin
- (d) Morphine

17. Receptors are proteins and crucial to body communication process. These receptors are embedded in

- (a) cell membrane
- (b) protein
- (c) endocrine gland
- (d) chromosomes.

18. Which of the following monomers form biodegradable polymers?

- (a) Ethylene glycol and phthalic acid
- (b) Caprolactum and 1, 3-butadiene
- (c) Phenol and formaldehyde
- (d) 3-Hydroxybutanoic acid and 3-hydroxypentanoic acid

19. Match the List-I with List-II in the following :

List-I		List-II	
I.	Caprolactum	(A)	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CH}_3 \end{array}_n$
II.	Vinyl chloride	(B)	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{C}_6\text{H}_5 \end{array}_n$
III.	Styrene	(C)	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{Cl} \end{array}_n$
IV.	Propene	(D)	$\begin{array}{c} \text{O} \\ \\ -\text{C}-(\text{CH}_2)_5\text{N}- \\ \\ \text{H} \end{array}_n$

- (a) I - (C), II - (D), III - (A), IV - (B)

- (b) I - (A), II - (D), III - (C), IV - (B)

- (c) I - (D), II - (C), III - (A), IV - (B)

- (d) I - (D), II - (C), III - (B), IV - (A)

20. The correct order of first ionisation enthalpy of given elements is

- (a) $\text{Li} < \text{B} < \text{Be} < \text{C}$
- (b) $\text{Be} < \text{Li} < \text{B} < \text{C}$
- (c) $\text{C} < \text{B} < \text{Be} < \text{Li}$
- (d) $\text{Li} < \text{Be} < \text{B} < \text{C}$

21. Which of the following statements is incorrect?

- (a) Bond length of $\text{O}_2 >$ Bond length of O_2^{2+}
- (b) Bond order of $\text{O}_2^+ <$ Bond order of O_2^{2-}
- (c) Bond length of $\text{O}_2 <$ Bond length of O_2^{2-}
- (d) Bond order of $\text{O}_2 >$ Bond order of O_2^{2-}

22. A gas at a pressure of 2 atm is heated from 25°C to 323°C and simultaneously compressed to $2/3^{\text{rd}}$ of its original value. Then the final pressure is

A		B	
P.	Molecular solid	(i)	SiC
Q.	Ionic solid	(ii)	Mg
R.	Metallic solid	(iii)	H_2O
S.	Network solid	(iv)	MgO

- (a) P-(iii), Q-(i), R-(ii), S-(iv)
 (b) P-(iv), Q-(iii), R-(ii), S-(i)
 (c) P-(ii), Q-(iv), R-(iii), S-(i)
 (d) P-(iii), Q-(iv), R-(ii), S-(i)
- 40.** A metal crystallises in a body centered cubic lattice with the metallic radius $\sqrt{3}$ Å. The volume of the unit cell in m^3 is
 (a) 64×10^{-29} (b) 4×10^{-29}
 (c) 6.4×10^{-29} (d) 4×10^{-10}
- 41.** The resistance of 0.1 M weak acid HA in a conductivity cell is 2×10^3 ohm. The cell constant of the cell is 0.78 C m^{-1} and λ_m° of acid HA is $390 \text{ S cm}^2 \text{ mol}^{-1}$. The pH of the solution is
 (a) 3.3 (b) 4.2 (c) 5 (d) 3
- 42.** In which one of the following reactions, rate constant has the unit $\text{mol L}^{-1} \text{ s}^{-1}$?
 (a) Acid catalysed hydrolysis of $\text{CH}_3\text{COOCH}_3$
 (b) $\text{CHCl}_3 + \text{Cl}_2 \longrightarrow \text{CCl}_4 + \text{HCl}$
 (c) $2\text{NO}_{(g)} + \text{O}_{2(g)} \longrightarrow 2\text{NO}_{2(g)}$
 (d) Decomposition of HI on the surface of gold
- 43.** For a reaction, the value of rate constant at 300 K is $6.0 \times 10^5 \text{ s}^{-1}$. The value of Arrhenius factor A at infinitely high temperature is
 (a) $6 \times 10^5 \times e^{-E_a/300R}$ (b) $e^{-E_a/300R}$
 (c) $\frac{6 \times 10^5}{300}$ (d) 6×10^5
- 44.** The rate constants k_1 and k_2 for two different reactions are $10^{16} \times e^{-2000/T}$ and $10^{15} \times e^{-1000/T}$ respectively. The temperature at which $k_1 = k_2$ is
 (a) $\frac{2000}{2.303} \text{ K}$ (b) 2000 K
 (c) $\frac{1000}{2.303} \text{ K}$ (d) 1000 K
- 45.** During the electrolysis of brine, by using inert electrodes,
 (a) O_2 liberates at anode
 (b) H_2 liberates at anode
 (c) Na deposits on cathode
 (d) Cl_2 liberates at anode.
- 46.** Consider the following 4 electrodes :
 A : $\text{Ag}^+(0.0001 \text{ M})/\text{Ag}_{(s)}$
 B : $\text{Ag}^+(0.1 \text{ M})/\text{Ag}_{(s)}$
 C : $\text{Ag}^+(0.01 \text{ M})/\text{Ag}_{(s)}$
 D : $\text{Ag}^+(0.001 \text{ M})/\text{Ag}_{(s)}$; $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$
- Then reduction potentials in volts of the electrodes in the order
 (a) B > C > D > A (b) C > D > A > B
 (c) A > D > C > B (d) A > B > C > D
- 47.** When FeCl_3 is added to excess of hot water gives a sol 'X'. When FeCl_3 is added to $\text{NaOH}_{(aq)}$ solution, gives sol 'Y'. X and Y formed in the above processes respectively are
 (a) $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{OH}^-$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{Fe}^{3+}$
 (b) $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{H}^+$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{Na}^+$
 (c) $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{Cl}^-$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{OH}^-$
 (d) $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{Fe}^{3+}$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{OH}^-$
- 48.** The reducing agent in the given equations :

$$4\text{Ag}_{(s)} + 8\text{CN}_{(aq)}^- + 2\text{H}_2\text{O}_{(aq)} + \text{O}_{2(g)} \longrightarrow 4[\text{Ag}(\text{CN})_2]_{(aq)}^- + 4\text{OH}_{(aq)}^-$$

$$2[\text{Ag}(\text{CN})_2]_{(aq)}^- + \text{Zn}_{(s)} \longrightarrow [\text{Zn}(\text{CN})_4]_{(aq)}^{2-} + 2\text{Ag}_{(s)}$$

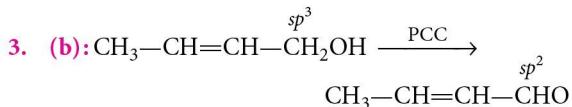
 (a) Zn (b) O_2 (c) H_2O (d) CN^-
- 49.** For the formation of which compound in Ellingham diagram ΔG° becomes more and more negative with increase in temperature?
 (a) CO (b) FeO (c) ZnO (d) Cu_2O
- 50.** Which of the following compound does not give dinitrogen on heating?
 (a) $\text{Ba}(\text{N}_3)_2$ (b) NH_4NO_2
 (c) NH_4NO_3 (d) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
- 51.** Aqueous solution of raw sugar when passed over beds of animal charcoal, it becomes colourless. Pick the correct set of terminologies that can be used for the above example.
- | | Adsorbent | Adsorbate | Process |
|-----|---------------------|---------------------|----------------|
| (a) | Solution of Sugar | Animal Charcoal | Sorption |
| (b) | Animal Charcoal | Solution of Sugar | Absorption |
| (c) | Animal Charcoal | Colouring substance | Adsorption |
| (d) | Colouring Substance | Animal Charcoal | Adsorption |
- 52.** For Freundlich adsorption isotherm, a graph of $\log(x/m)$ vs. $\log(P)$ gives a straight line. The slope of line and its Y-axis intercept respectively are

- (a) $\log\left(\frac{1}{n}\right), K$ (b) $\frac{1}{n}, \log K$
 (c) $\log\left(\frac{1}{n}\right), \log K$ (d) $\frac{1}{n}, K$
53. In solid state, PCl_5 is a/an
 (a) octahedral structure
 (b) ionic solid with $[\text{PCl}_6]^{+}$ and $[\text{PCl}_4]^{-}$
 (c) ionic solid with $[\text{PCl}_4]^{+}$ and $[\text{PCl}_6]^{-}$
 (d) covalent solid present in the form of P_2Cl_{10} .
54. In which one of the following pairs, both the elements does not have $(n-1)d^{10}ns^2$ configuration in its elementary state?
 (a) Zn, Cd (b) Cd, Hg
 (c) Hg, Cn (d) Cu, Zn
55. Which of the following is correct with respect to melting point of a transition element?
 (a) V > Cr (b) Cr > Mn
 (c) Mn > Fe (d) Ti > V
56. $a\text{MnO}_4^- + b\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow x\text{MnO}_2 + y\text{SO}_4^{2-} + z\text{OH}^-$
 a and y respectively are
 (a) 8; 3 (b) 8; 6 (c) 3; 6 (d) 8; 8
57. Which formula and name combination is incorrect?
 (a) $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]^-$ – Potassium trioxalatoaluminate (III)
 (b) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]^-$ – Diamminechloridonitrito-N-platinum(II)
 (c) $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ – Dichloridodiethylenediamminecobalt(II) chloride
 (d) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2^-$ – Tetraammineaquachloridocobalt(III) chloride
58. Which of the following system in an octahedral complex has maximum unpaired electrons?
 (a) d^9 (high spin) (b) d^6 (low spin)
 (c) d^4 (low spin) (d) d^7 (high spin)
59. The correct decreasing order of basicity of hydrides of Group-15 elements is
 (a) $\text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$
 (b) $\text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{NH}_3$
 (c) $\text{AsH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{PH}_3$
 (d) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$
60. Which one of the following oxoacids of phosphorus can reduce AgNO_3 to metallic silver?
 (a) H_3PO_2 (b) $\text{H}_4\text{P}_2\text{O}_7$
 (c) $\text{H}_4\text{P}_2\text{O}_6$ (d) H_3PO_4

SOLUTIONS

1. (d): (+) Butan-2-ol and (-) butan-2-ol are enantiomers. Enantiomers have identical chemical and physical properties. They have different directions of rotation of the plane of polarised light.

2. (a)



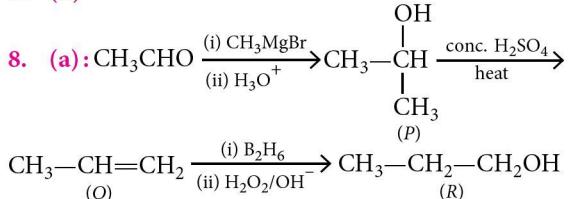
Hybridisation at C-1 is changed from sp^3 to sp^2 .

4. (d)

5. (b): Compounds in which metal is directly attached with carbon are called organometallic compounds.

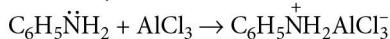
6. (a): PCC (pyridinium dichromate) is used to oxidise primary alcohols to aldehydes.

7. (d)



(P) and (R) are position isomers.

9. (c): Aniline is a Lewis base while AlCl_3 is a Lewis acid. They combine with each other to form a salt.



Due to the presence of a positive charge on N-atom in the salt, the group $-\dot{\text{N}}\text{H}_2\overset{+}{\text{AlCl}_3}^-$ acts as a strong electron-

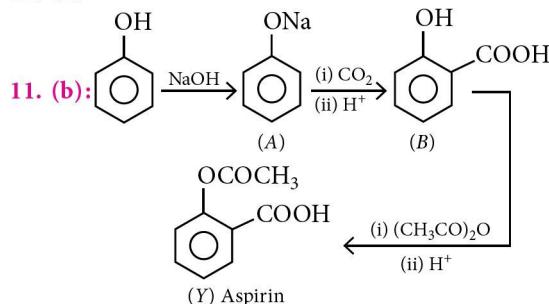
SOLUTIONS TO JUNE 2023 QUIZ CLUB

- | | |
|-------------------------|-------------------------------|
| 1. Calcium hypochlorite | 11. Diffusion |
| 2. 10 | 12. Separating funnel |
| 3. Chloramphenicol | 13. Hafnium |
| 4. 15 | 14. Acetylene |
| 5. Intrinsic | 15. Nitric acid |
| 6. Potassium nitrate | 16. Global warming |
| 7. Anode | 17. Overvoltage/Overpotential |
| 8. Glycerol | 18. Amylase |
| 9. Quinine | 19. Copper matte |
| 10. Goitre | 20. Carbon monoxide |

Winner: Kaushikumar Kevadiya

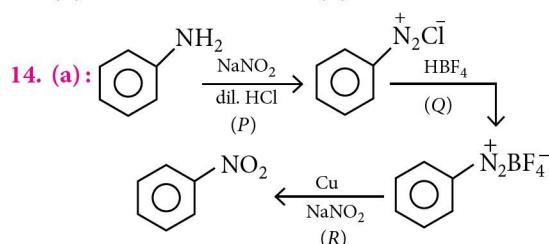
withdrawing group. As a result, it reduces the electron density on the benzene ring. For this reason, aniline does not undergo Friedel–Crafts reaction.

10. (d)



12. (d)

13. (d)



15. (c)

16. (c): Heroin, codeine and morphine are narcotic analgesics. Aspirin is a non-narcotic analgesic.

17. (a): Receptors are proteins that are crucial to body's communication process. Majority of these are embedded in cell membranes.

18. (d): 3-Hydroxybutanoic acid and 3-hydroxypentanoic acid form biodegradable polymer PHBV.

19. (d)

20. (a): In general, along a period, the ionisation enthalpy increases with increase in atomic number and decrease in atomic size. Among the given elements of the second period, C is smallest among the four. Hence, it has highest ionisation enthalpy. Electron in Be has to be removed from filled $2s$ orbital which is more energy demanding than B, in which electron has to be removed from $2p$ orbital. Li has smallest ionisation enthalpy due to greater size.

21. (b): Bond order of $O_2 = 2$, $O_2^+ = 2.5$, $O_2^{2+} = 3$, $O_2^{-} = 1$. Bond length is in the order $O_2^{2-} > O_2 > O_2^+ > O_2^{2+}$

22. (b)

23. (b): Enthalpy of solution

$$\begin{aligned} &= \text{Lattice enthalpy} + \text{Hydration enthalpy} \\ &= (788 - 784) \text{ kJ mol}^{-1} = +4 \text{ kJ mol}^{-1} \end{aligned}$$

24. (d): Equilibrium constant depends only on temperature.

$$\begin{aligned} \text{25. (d): } \text{pH} &= \frac{1}{2} (\text{p}K_w + \text{p}K_a - \text{p}K_b) \\ &= \frac{1}{2} (14 + 5.9 - 5.8) = 7 + 0.05 = 7.05 \end{aligned}$$

$$\begin{aligned} \text{26. (a): } {}^\circ\text{F} &= \frac{9}{5}({}^\circ\text{C}) + 32 = \left(\frac{9}{5} \times 25\right) + 32 \\ &= 45 + 32 = 77 \end{aligned}$$

$$25^\circ\text{C} = (273.15 + 25) \text{ K} = 298.15 \text{ K}$$

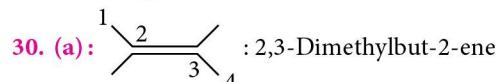
$$\text{27. (b): } {}^{32}\text{S}^{2-} : \text{No. of protons} = 16$$

$$\text{No. of electrons} = 16 + 2 = 18$$

$$\text{No. of neutrons} = (32 - 16) = 16$$

28. (d): BeO and ZnO are amphoteric oxides.

29. (d): Mixture of carbon monoxide and hydrogen is called water gas.



31. (d): I, II and IV are aromatic species as they follow Huckel's rule of aromaticity.

32. (a): CO binds more easily with haemoglobin than O_2 , and forms carboxy haemoglobin.

33. (d)

34. (d): Volume strength =

$$\frac{5.6 \times \text{Percentage strength} \times 10}{\text{Equivalent weight of H}_2\text{O}_2} = \frac{5.6 \times 30 \times 10}{17} = 98.82 \approx 100$$

A 30% solution of H_2O_2 is 100 volume H_2O_2 .

35. (b): In simple cubic system, $2r = a$; $r = \frac{a}{2}$

In body centered cubic system, $4r = \sqrt{3}a$; $r = \frac{\sqrt{3}a}{4}$

In face centered cubic system, $4r = \sqrt{2}a$

$$\text{or } r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}}$$

36. (a)

37. (b)

38. (a): Let van't Hoff factor for AB be i .

$$\alpha = \frac{i-1}{n-1}; 0.8 = \frac{i-1}{2-1}; 0.8 = i-1; i = 1.8$$

Let van't Hoff factor for XY_2 be i' .

$$\alpha' = \frac{i'-1}{n-1}; 0.6 = \frac{i'-1}{3-1}; i'-1 = 1.2; i' = 2.2$$

$$\Delta T_f = iK_f m_1 + i'K_f m_2$$

$$= \left(1.8 \times K_f \times \frac{5.85 \times 1000}{58.5 \times 94.15} \right) + \left(2.2 \times K_f \times \frac{9.5 \times 1000}{95 \times 90.5} \right)$$

$$= K_f (1.91 + 2.43) = 1.86 \times 4.34 = 8.07$$

The freezing point of water will be = $(273 - 8.07)$
 $= 264.93\text{ K}$

39. (d)

40. (c): For *bcc* lattice, $a = \frac{4r}{\sqrt{3}}$

$$\text{Volume of unit cell} = a^3 = \left(\frac{4r}{\sqrt{3}} \right)^3 = \frac{64r^3}{3\sqrt{3}}$$

$$= \frac{64 \times (\sqrt{3} \times 10^{-8})^3}{3\sqrt{3}} \text{ cm}^3 = 64 \times 10^{-24} \text{ cm}^3$$

$$= 6.4 \times 10^{-29} \text{ m}^3$$

$$\text{41. (d): } \Lambda_m = \frac{1000 \times \kappa}{C} = \frac{1000 \times 0.78}{0.1 \times 2 \times 10^3} = 3.9$$

$$\left(\kappa = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{0.78}{2 \times 10^3} \right)$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{3.9}{390} = 0.01$$

$$\text{pH} = -\log[\text{H}^+] = -\log[\text{Ca}] = -\log[0.1 \times 0.01] \\ = -\log(10^{-3}) = 3$$

42. (d): Mol L⁻¹ s⁻¹ is the unit of zero order rate constant. Decomposition of HI on gold surface is a zero order reaction.

43. (d): $k = Ae^{-E_a/RT}$ (Arrhenius equation)

$$A = ke^{E_a/RT} \text{ at } T = \infty, \frac{1}{T} = 0$$

$$\therefore A = k$$

$$A = 6 \times 10^5$$

44. (c)

45. (d): During electrolysis of brine solution, H₂ liberates at cathode, while Cl₂ liberates at anode.

$$\text{46. (a): A. } E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{1} \log \frac{1}{0.0001}$$

$$= 0.8 - 0.059 \log 10^4 = 0.8 - 0.059 \times 4 = 0.564 \text{ V}$$

$$\text{B. } E_{\text{cell}} = 0.8 - 0.059 \log \frac{1}{0.1} = 0.8 - 0.059 = 0.741 \text{ V}$$

$$\text{C. } E_{\text{cell}} = 0.8 - 0.059 \log \frac{1}{0.01} = 0.8 - 0.059 \times 2 = 0.682 \text{ V}$$

$$\text{D. } E_{\text{cell}} = 0.8 - 0.059 \log \frac{1}{0.001} = 0.8 - 0.059 \times 3 \\ = 0.623 \text{ V}$$

\therefore The correct order is B > C > D > A.

47. (d)

48. (a): Zn is reducing agent as it itself getting oxidised to Zn²⁺ and reduces Ag⁺ to Ag.

49. (a)



51. (c): Colouring substance \rightarrow Adsorbate

Animal charcoal \rightarrow Adsorbent

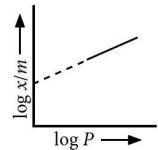
Process \rightarrow Adsorption

52. (b): Freundlich adsorption isotherm :

$$\frac{x}{m} = KP^{1/n}$$

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log P$$

$$\log \frac{x}{m} = \frac{1}{n} \log P + \log K$$



In a graph of $\log x/m$ vs. $\log P$,

$1/n$ = slope and $\log K$ = intercept

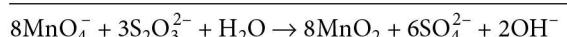
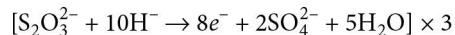
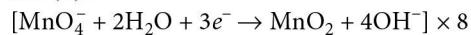
53. (c): In the solid state, PCl₅ exists as ionic solid, [PCl₄]⁺ [PCl₆]⁻.

54. (d): Cu : 3d¹⁰ 4s¹

Zn : 3d¹⁰ 4s²

55. (b): Melting point of Mn < Cr.

56. (b):



$$a = 8, y = 6.$$

57. (c): [CoCl₂(en)₂]Cl – Dichloridobis(ethylene diammine)cobalt(III) chloride

58. (d): d⁷ (high spin) has 3 unpaired electrons.

d⁹ (high spin) has 1 unpaired electron.

d⁶ (low spin) has no unpaired electron.

d⁴ (low spin) has 2 unpaired electrons.

59. (d) : As the size of the central atom increases, the electron density on the central atom decreases and consequently, its tendency to donate a pair of electrons decreases. Hence, the basicity decreases from NH₃ to BiH₃.

60. (a): Oxoacid having P–H bond acts as reducing agent. Among the given oxoacids of phosphorus, only H₃PO₂ has P–H bond.





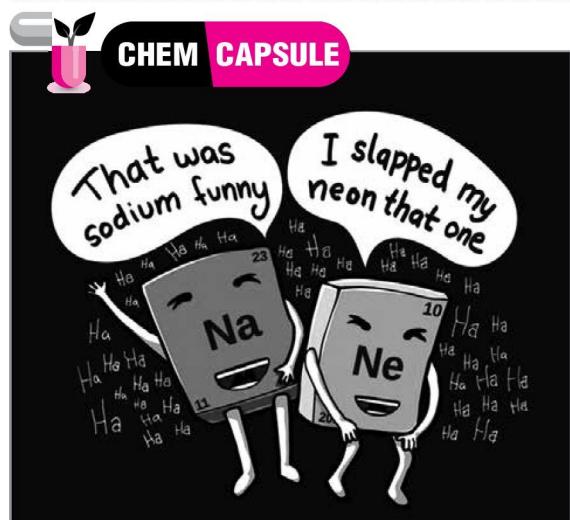
Unlock Your Knowledge!



1. Isotopes of an element differ in their number of _____.
_____.
2. The allotrope of carbon that occurs in a solid three-dimensional structure is _____.
_____.
3. A sulpha drug that is used to cure pneumonia is _____.
_____.
4. A condensation polyamide that is used in protective clothing for fire resistance is _____.
_____.
5. A vitamin whose deficiency causes pyorrhea and scurvy is _____.
_____.
6. The process in which chlorobenzene is infused with NaOH at 623 K and 300 atm pressure to produce phenol is called _____.
_____.
7. A basic magnesium carbonate that is used as a dental abrasive and in cosmetics is _____.
_____.
8. The bond order of C₂ molecule is _____.
_____.
9. A system in which there is no exchange of matter, work or energy from the surroundings is said to be _____.
_____.
10. A chemical reaction in which two reactants containing the same element with different oxidation numbers, form a compound having an intermediate oxidation number is called _____.
_____.
11. The number of resonance structures of carbonate ion is _____.
_____.
12. The number of lone pairs on the central atom in SF₆ is _____.
_____.
13. When the reaction quotient is less than the equilibrium constant, the reaction proceeds in the _____ direction.
_____.
14. F₂ is a stronger _____ agent as compared to Cl₂.

15. Generally, _____ show -1 oxidation state in most of their compounds.
_____.
16. The amount of energy released when an electron is added to an isolated gaseous atom of the element is called _____.
_____.
17. The ratio of mass of hydrogen to the mass of oxygen in water is _____.
_____.
18. The number of unpaired d-electrons in Fe²⁺ ion is _____.
_____.
19. Ethylene glycol and phthalic acid are the monomer units of a polymer called _____.
_____.
20. _____ is used as a substitute for wool in making commercial fibres such as acrilan.

◆◆
Readers can send their responses at editor@mtg.in or post us with complete address by 10th of every month. Winners' names and answers will be published in next issue.



GK CORNER

Enhance Your General Knowledge with Current Updates!



INTERNATIONAL NEWS

- **The International Conference on Spacecraft Mission Operations (SMOPS-2023)** : It was organised by the Indian Space Research Organisation (ISRO) in collaboration with the Italian Space Agency (ASI) and the International Academy of Astronautics (IAA). SMOPS-2023 aims to bring together experts from space agencies, start-ups, industry and academia to discuss emerging technologies and automation in space mission operations and ground segment.
- **G7 summit** : The 49th G7 summit, held from 19th to 21st May 2023, was hosted by Hiroshima, Japan. The choice of Hiroshima as the host city of the G7 Summit underlines Prime Minister Kishida's commitment to put nuclear disarmament and non-proliferation prominently on the agenda of the meeting. Indian Prime Minister Narendra Modi also attended the Summit at the invitation of Japanese Prime Minister.
- **The India-EU Connectivity Conference** was jointly organised by the Ministry of External Affairs (MEA), the EU Delegation to India, and leading think-tank Asian Confluence, in Meghalaya from 1st to 2nd June. The conference aimed to explore opportunities for enhancing connectivity investments in India's North Eastern States and its neighbouring countries including Nepal, Bhutan and Bangladesh.
- The UAE government launched the '**Machines Can See 2023**' Summit, one of the international conferences in Artificial Intelligence (AI) held at the Museum of the Future in Dubai. It aimed to bring together experts from around the world to discuss the future of AI and its potential in contributing to the UAE's vision of creating the next Silicon Valley.
- **Global Wealth Conference (GWC)** : The Sovereign Wealth Fund Institute (SWFI) organised the highly anticipated event in the financial world in London from 31st May to 1st June 2023. It brought together some of the world's largest investors, including sovereign wealth funds, pensions, foundations, official institutions, endowments, large family offices and other asset owners with top-level industry leaders.
- The **6th Indian Ocean Conference** was held on 12th-13th May 2023 in Dhaka, Bangladesh with the theme "Peace Prosperity and Partnership for a Resilient Future". Over 25 countries participated in this conference and discussed the ways to promote economic development while maintaining peace and stability in the region.
- The Prime Minister of Singapore, Lee Hsien Loong attended the 42nd ASEAN Summit from 10th to 11th May 2023 in Labuan Bajo, Indonesia. The Leaders reviewed ASEAN's progress and discussed ways to further enhance collaboration in the digital and green economies. They also discussed the geopolitical situation, with the view to maintain ASEAN's central role in an open, inclusive and stable regional architecture.
- **World Health Assembly 2023** : The 76th session was held with the theme "Saving lives, driving health for all", at World Health Organisation Headquarters,

Geneva from 21st to 30th May 2023. The World Health Assembly (WHA) is WHO's decision-making body and it is attended by delegations from all of WHO member states and focuses on a specific health agenda prepared by the Executive Board.

- **Arab League Summit 2023 :** It was recently concluded in Jeddah, Saudi Arabia, with the adoption of the Jeddah declaration. This declaration focuses on fostering Arab unity and addressing various regional challenges. An important highlight of the summit was the unanimous decision to readmit Syria to the Arab League. The declaration emphasizes the need for increased pan-Arab efforts to assist Syria in resolving its ongoing crisis, demonstrating a collective commitment to support stability and peace in the country.

- **Quad Leaders' Summit :** Prime Minister Shri Narendra Modi participated in the third in-person Quad Leaders' Summit in Hiroshima, Japan on 20th May 2023, along with Prime Minister of Australia, Anthony Albanese, Prime Minister of Japan, Fumio Kishida and President of the United States of America, Joseph Biden.
- **SAI20 Summit :** The Comptroller and Auditor General of India is the Chair of the Supreme Audit Institutions-20 (SAI20) Engagement Group under India's G20 Presidency. The SAI20 Summit took place in the state of Goa from 12th to 14th June 2023. The delegates from SAI20 member SAIs of G20 countries, Guest SAIs, Invited SAIs, International Organizations, Engagement Groups and other invitees attended the SAI20 Summit.

Test Yourself!

1. In 2023, the World Health Assembly was held in
 - (a) Geneva
 - (b) Paris
 - (c) London
 - (d) Brussels
2. Who is the Chair of SAI20 Engagement Group?
 - (a) Comptroller and Auditor General of India
 - (b) Finance Minister
 - (c) RBI Governor
 - (d) Chief Audit Executive
3. Which of the following represents the correct listing of QUAD group nations?
 - (a) India, Japan, China and Australia
 - (b) India, Japan, UK and China
 - (c) India, Japan, Canada and UK
 - (d) India, Japan, USA and Australia
4. Which of the following countries had the Chairmanship of ASEAN for 2023?
 - (a) Brunei
 - (b) Cambodia
 - (c) Philippines
 - (d) Indonesia
5. What was the theme for 6th Indian Ocean Conference?
 - (a) Peace Prosperity and Partnership for a Resilient Future
 - (b) Scaling up Ocean Action based on Science and Innovation
 - (c) Invest in Our Oceans
 - (d) Our Oceans Our Future
6. Which of the following nations hosted the 'Machines Can See 2023' Summit?
7. The 49th G7 summit is hosted by the Prime Minister
 - (a) Anthony Albanese
 - (b) Pushpa Kamal Dahal
 - (c) Fumio Kishida
 - (d) Rishi Sunak
8. Who organised the event of Global Wealth Conference (GWC)?
 - (a) Institute of International Finance
 - (b) Sovereign Wealth Fund Institute
 - (c) International Monetary Fund
 - (d) World Bank
9. Which of the following countries was admitted to the Arab League in its 32nd Ordinary Session of the Council of the League of Arab States?
 - (a) Iraq
 - (b) Kuwait
 - (c) Qatar
 - (d) Syria
10. Which of the following organisations organised the International Conference on Spacecraft Mission Operations 2023?
 - (a) Indian Space Research Organisation
 - (b) International Science Council
 - (c) Council of Scientific and Industrial Research
 - (d) Department of Science and Technology

Answer Key

- | | | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|
| 1. (a) | 2. (a) | 3. (d) | 4. (d) | 5. (a) | 6. (d) | 7. (c) | 8. (b) | 9. (d) | 10. (a) |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|





Unique Career in Demand

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B. Tech. Ceramic Engineering

- Ceramic Engineering is the science and technology of creating objects from inorganic and non-metallic materials. It is one of the new engineering specialties that is associated with the production as well as generation of ceramic commodities for use in various industries.
- B. Tech. in Ceramic Engineering is a four-year undergraduate engineering degree programme where students get to study different kinds of ceramic substances and a number of approaches to generate and crystallise them. It also covers the utility of ceramic materials in the chemical, mechanical and electrical engineering.

Entrance Exams

- JEE Main
- CUET
- MHT CET
- WBJEE

Top Colleges

- Government College of Engineering and Ceramic Technology, Kolkata**
- Indian Institute of Technology (BHU), Varanasi
- National Institute of Technology, Rourkela
- P.D.A. College of Engineering, Kalaburagi

Eligibility

Admission to the course of B. Tech. in Ceramic Engineering requires the eligible aspirants to pass Class 12 in PCM or PCB stream with a minimum of 45-50% of marks. Most of the colleges and universities require candidates to take entrance exams.

Career

- A ceramic engineer can easily find employment in sectors like ceramicware manufacturing units, kitchenware industry, research and testing firms, tableware and sanitaryware industries, cutting tools industry and others. A ceramic engineer can operate in research labs and hospitals as well.
- Ceramic engineers can be hired in aerospace, electronics, packaging science, mining, food and chemical industries.
- Ceramic engineers can also prepare for exams to serve in esteemed organisations such as ISRO, BARC, etc.
- After a few years of gaining skills and experience, engineers/technologists can also opt for entrepreneurship and start their own businesses.

Government College of Engineering and Ceramic Technology, Kolkata

Formerly known as College of Ceramic Technology (CCT), it is a public college affiliated to the Maulana Abul Kalam Azad University of Technology (MAKAUT) in Kolkata with 80 years of existence. There is an intake capacity of 48 students (40 through WBJEE and 8 through JELET respectively) per department. The GCECT can boast of well-equipped workshop and laboratories, which is essential for the scheduled academic curriculum and research activities operational at the institute such as the Thin Film lab, Nano-Materials and Sol-gel Lab of the Ceramic Department. The institute library has more than 17,000 books as well as 15 or more National and International Journals covering various arenas of research and study. The entire campus is connected to the internet for 24 hours through NKN Leased Line (100 mbps) connectivity which is accessible from all computers in the institute. The institute has also received grant from the World Bank in the TEQIP One Phase for various developmental projects. The Institute has collaborated with reputed institutions at national and international level for postgraduate, project and Ph.D. programmes like The Petronas University of Malaysia, Northern University in Saudi Arabia, etc. The final year students of Ceramic Technology have already undergone 100% recruitment in various renowned companies like Saint Gobain Glass, Jindal South West Steel, Essar Steel, Steel Authority of India, Grindwell Norton, MECON, Tata Refractories Ltd. and more.



Official Website : <https://gcet.ac.in/>

UNSCRAMBLE ME

Unscramble the words given in column I and match them with their explanations in column II.

Column I	Column II
1. HEMICUMLENICENSEC	(a) A group of atoms in a molecule which is responsible for the colour of the compound.
2. EDIMAANITNO	(b) A monosaccharide sugar that has a five-component cyclic structure containing one oxygen atom and four carbon atoms.
3. HROCOMHPEOR	(c) It is a chief ore of lead that usually occurs as grey metallic cubes.
4. PLAELEROTCGTIN	(d) It is the emission of light from a chemical reaction.
5. URFONAES	(e) The removal of an amino group from an amino acid or other compound.
6. ALGAEN	(f) It is defined as the process of coating a very thin layer of one metal over the surface of other by means of electrolysis.
7. RANLAGUITNO	(g) It is defined as the atom with a particular number of protons and neutrons.
8. UCNILDE	(h) It is a polymer used in making disposable cups and packaging materials.
9. RATNIUQILEZRS	(i) The process that involves the size reduction and size enlargement for producing granules.
10. OPYLSTREYEN	(j) A class of drugs that are useful in the treatment of stress and mild or several mental diseases.

Readers can send their responses at editor@mtg.in or post us with complete address by 10th of every month.
Winners' names and answers will be published in next issue.

Chemistry in

Class 11 & 12

FOCUS

TOPIC

Substitution Reactions

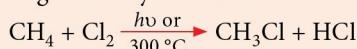
Detailed theory with High Definition images of the given topic is covered under this heading.

Substitution reactions are the reactions in which an atom or group of an organic molecule is replaced by another atom or group without any change in the remaining part of the molecule. Depending upon the nature of attacking reagent, substitution reactions are of following types :

Free Radical Substitution

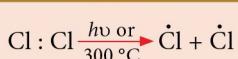
A free radical substitution reaction is defined as the substitution reaction wherein the reactive intermediate is a free radical. These reactions are initiated by radicals in the gas phase or in non-polar solvents.

Consider the following example that involves the reaction of methane and chlorine in the presence of sunlight or heat to produce methyl chloride. Light energy or heat results in the homolytic fission of chlorine producing chlorine radicals that attack methane to give methyl chloride.



Mechanism of free radical substitution of CH_4

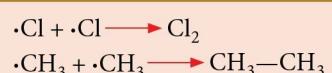
Initiation



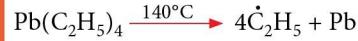
Propagation



Termination



The mechanism is supported by the fact that no reaction takes place in the dark, and in the presence of tetraethyl lead (0.02%), the reaction occurs at 140°C. Tetraethyl lead decomposes at 140°C to ethyl radical that produces chlorine radical from chlorine for the propagation of the reaction.

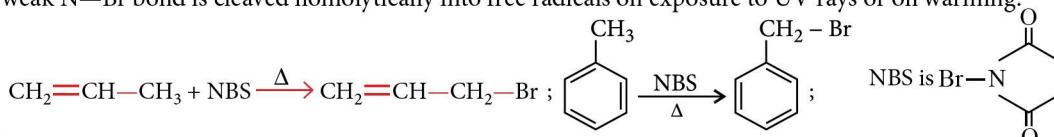


When the ratio of methane to chlorine is high, methyl chloride is formed predominantly and when chlorine is in excess, all the hydrogens are replaced to give carbon tetrachloride.

Halogenation of simple alkanes in presence of sunlight generally follows free radical mechanism. Reactivity of halogens for free radical substitution is in order : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

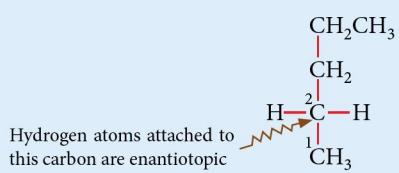
For a given halogen, ease of abstraction of hydrogen follows the order : $(\text{C}_6\text{H}_5)_3\dot{\text{C}} > (\text{C}_6\text{H}_5)_2\dot{\text{C}}\text{H} > \text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2 > \text{CH}_2 = \text{CH} - \dot{\text{C}}\text{H}_2 > (\text{CH}_3)_3\dot{\text{C}} > (\text{CH}_3)_2\dot{\text{C}}\text{H} > \text{CH}_3\dot{\text{C}}\text{H}_2 > \dot{\text{C}}\text{H}_3 > \text{CH}_2 = \dot{\text{C}}\text{H} > \text{HC} \equiv \dot{\text{C}}$

Abstraction of allylic hydrogen or benzylic hydrogen takes place using NBS (N-bromosuccinimide) in which weak N—Br bond is cleaved homolytically into free radicals on exposure to UV rays or on warming.

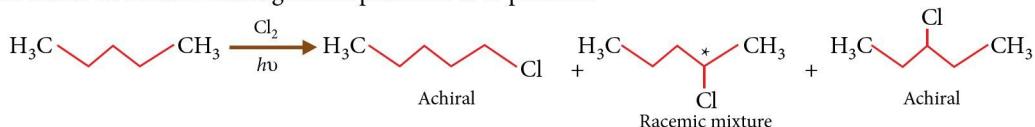


Generation of Stereocentre

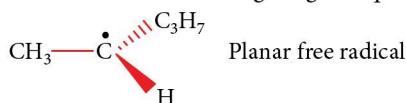
Consider *n*-pentane, the two hydrogen atoms attached to C² are enantiotopic; replacement of each in turn by some other atom or group leads to a pair of enantiomers.



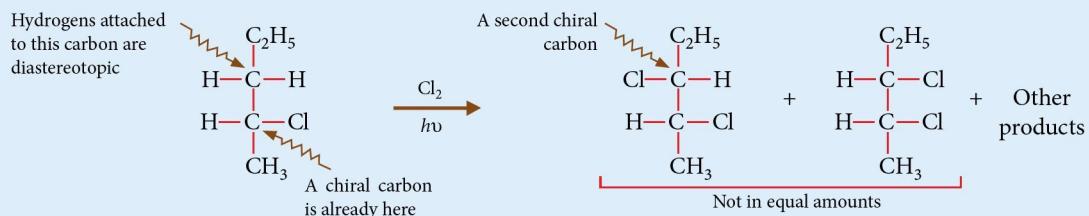
What happens during halogenation at this centre? Will it produce only one enantiomer or a racemic mixture? Let us check all the monohalogenated products of *n*-pentane.



The formation of racemic mixture implies that the radical intermediate produced in this reaction is planar. This planar radical then reacts with chlorine at either face giving an equal amount of *d* and *l* forms.



Now, we will discuss the case where the substrate contains diastereotopic hydrogens; replacement of each in turn leads to a pair of diastereomers. Consider the photochlorination of 2-chloropentane. Note that this substrate already has a chiral carbon. Monochlorination of this substrate gives rise to a pair of diastereomers, but not in equal amounts. The intermediate radical itself is chiral and the reaction takes place to a great extent on one face than the other.



Nucleophilic Substitution

A nucleophilic substitution reaction involves the displacement of a leaving group by a nucleophile. These reactions are of great commercial importance. Basic, electron rich reagents that have a tendency to attack the nucleus of carbon atom are known as nucleophilic reagents or simply nucleophiles. When this attack results in substitution, the reaction is termed as nucleophilic substitution.

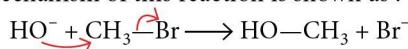


Consider the example of the hydrolysis of methyl bromide. When methyl bromide reacts with sodium hydroxide in a solvent that dissolves both reagents, methanol and sodium bromide are obtained. This is a substitution reaction as the —Br group is substituted by —OH in the original compound. In this reaction, an alkyl halide gets converted into an alcohol.



In the nucleophilic substitution reaction of methyl bromide with sodium hydroxide, the departing halide ion takes with it the electron pair it has been sharing with carbon; whereas the OH^- ion brings with it the electron pair which binds it to the carbon atom.

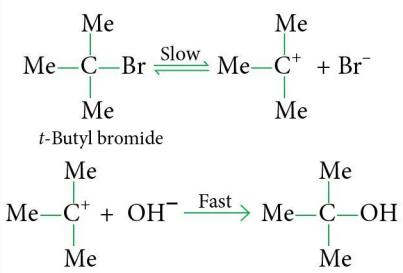
With formulas where a bond is depicted by a line instead of a pair of dots, curved arrows are used to indicate the movement of electrons, the mechanism of this reaction is shown as :



Investigations by Ingold and co-workers show that nucleophilic substitution reactions can take place by two different paths which have been designated by Ingold as S_N1 and S_N2 depending on the nucleophile, nature of the substrate, the leaving group and the solvent. Now, let us discuss these two types of nucleophilic substitution reactions in detail.

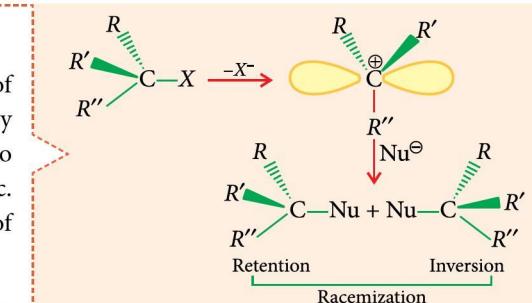
S_N1 Mechanism

Kinetic studies of the hydrolysis of *t*-butyl bromide show that the rate of the reaction is directly proportional to the concentration of the alkyl halide, *i.e.*, rate $\propto [R_3CX]$. As the rate of reaction depends on one of the reactants, the reaction is a first-order reaction. Nucleophilic substitution reaction that follows first-order kinetics is termed as S_N1 (Substitution Nucleophilic Unimolecular). Since the rate of reaction is independent of $[\text{OH}^-]$, it can be interpreted that the halide undergoes slow ionization in the first step resulting in the formation of a carbocation intermediate. In the second step, a fast attack of OH^- on the carbocation completes the hydrolysis.



Stereochemistry of S_N1 reactions

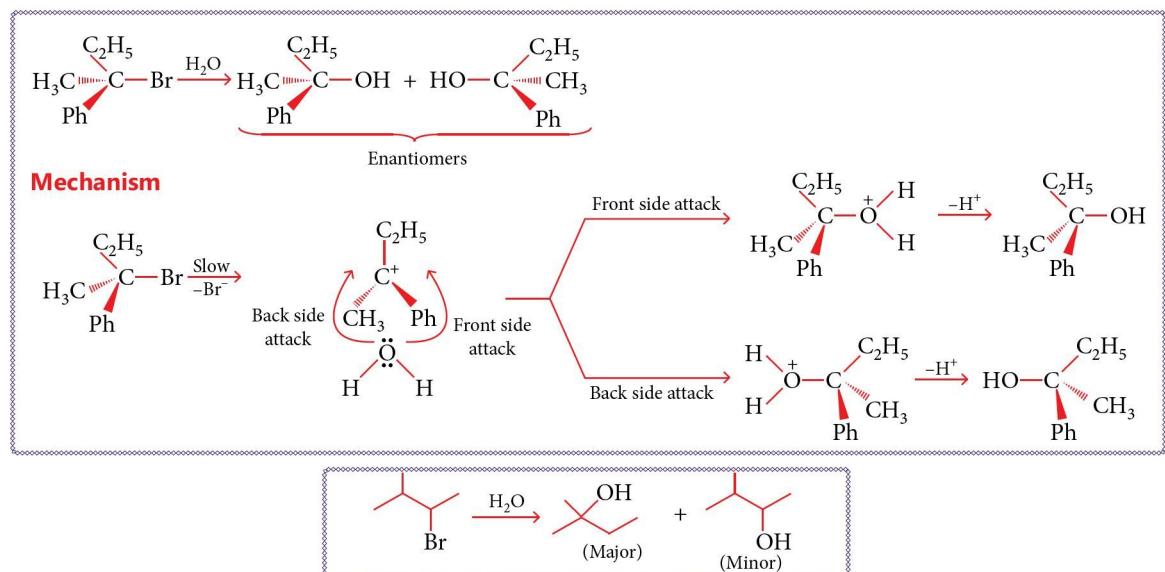
Carbonium ion intermediate produced in the course of S_N1 reaction has a planar structure. It can be attacked by the nucleophilic reagent from either side to produce two isomers *d* and *l* if the starting alkyl halide is asymmetric. Thus, a racemic mixture is obtained due to formation of equal amount of *d* and *l* forms and optical activity is lost.



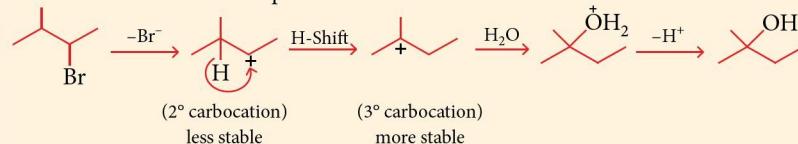
Rate of S_N1 reactions

- Order of reactivity of various alkyl halides towards S_N1 reaction is : $(\text{CH}_3)_3\text{CX} > \text{C}_6\text{H}_5\text{CH}_2\text{X} > \text{CH}_2 = \text{CHCH}_2\text{X} > (\text{CH}_3)_2\text{CHX} > \text{CH}_3\text{CH}_2\text{X} > \text{CH}_3\text{X}$
- This order follows the order of stability of carbocations. Leaving group breaks away as a base. Less basic the substituent, more easily it is displaced. The ease of separation of halide ions is in the order: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$, since carbon halogen bond strength follows the order : $\text{C}-\text{F} > \text{C}-\text{Cl} > \text{C}-\text{Br} > \text{C}-\text{I}$.
 \therefore A better leaving group increases the rate of S_N1 reactions.
- Nature of nucleophile does not alter the rate of S_N1 reaction since the rate determining step is ionization of the substrate.
- Polar protic solvents are found to be good for S_N1 reactions.

Examples of S_N1 reactions



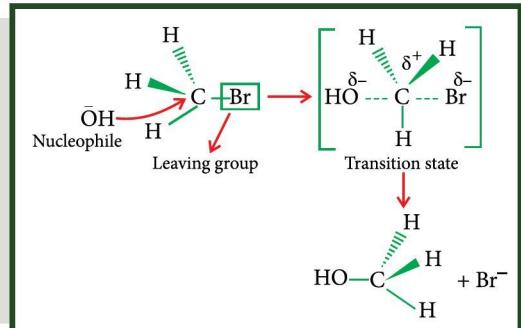
A carbocation intermediate is formed in an S_N1 reaction and the carbocation will rearrange to become more stable in the process. If the carbocation formed in an S_N1 can rearrange, the S_N1 reaction of the same alkyl halide can form different structural isomer products.



S_N2 Mechanism

Nucleophilic substitution reactions that follow second-order kinetics are called S_N2 (Substitution Nucleophilic Bimolecular) reactions. The rate of these reactions depends upon the concentrations of both the reactants. Hence, the rate of hydrolysis of methyl bromide with NaOH has been found to be of second order, *i.e.*, the rate $\propto [CH_3Br] [OH^-]$.

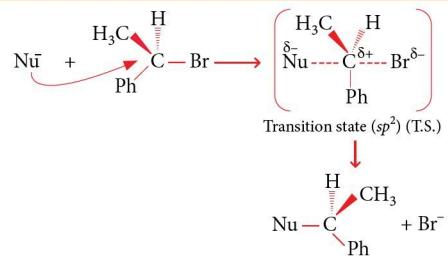
As the rate-determining step involves both CH₃Br and OH, a collision between the two reactants resulting in the direct displacement of Br by OH takes place in such a way that when a new C—OH bond is being formed, the old C—Br bond starts breaking, *i.e.*, the bond formation and the bond breaking processes are simultaneous. Thus, the reaction is a concerted one-step reaction without any intermediate.



Thus, it can be said that in an S_N2 mechanism a bond starts forming between carbon and attacking nucleophile at the same time as the bond between carbon and leaving group starts weakening. In the transition state, carbon is partially bonded to both attacking nucleophile as well as leaving group. When the carbon-nucleophile bond is completely formed, the carbon-leaving group bond is completely broken.

Stereochemistry of S_N2 reactions

In S_N2 reactions, the nucleophile attacks the side of the carbon atom opposite to that of the leaving group and yields a product whose configuration is opposite to that of the substrate. Thus, we can say that S_N2 reaction proceeds with stereochemical inversion known as **Walden inversion**.

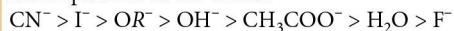


Rate of S_N2 reactions

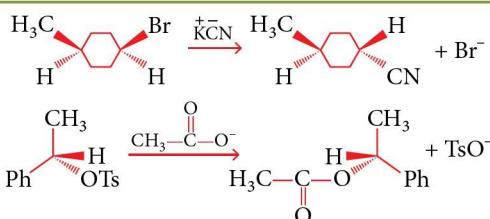
More bulky the groups attached to carbon-atom undergoing displacement, lesser will be the reactivity towards S_N2 reactions.



Rate of S_N2 reaction also depends upon the strength of attacking nucleophile. Strength of some common nucleophiles is in the order :



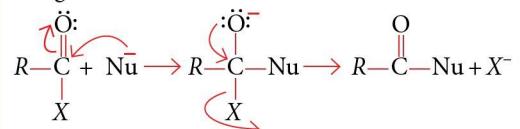
Examples of S_N2 reactions



At unsaturated carbon

When a carbon atom having multiple bonds with a heteroatom (e.g., N, O, S, etc.) is connected to a good leaving group like —Cl, —OH, —OR, —NH₂, etc., the nucleophilic attack on the carbon results in substitution rather than addition.

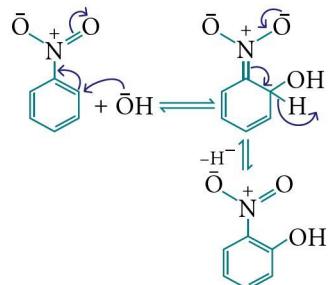
The general mechanism of the reactions is :



Nucleophiles can be $\bar{\Omega}\text{H}$, $R\ddot{\Omega}\text{H}$, $\ddot{\Omega}\text{H}_3$, etc.
 X can be Cl, NH₂, OH, OR, etc.

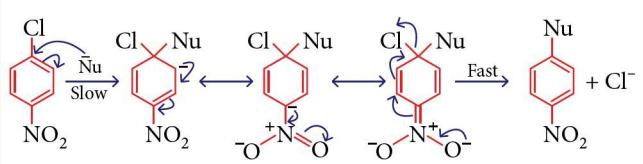
Nucleophilic Aromatic Substitution

Nucleophilic substitution of the hydrogen of benzene is difficult because (i) the π -electron cloud repels the nucleophile and (ii) it will be difficult for the ring to accommodate the negative charge brought in by the nucleophile. But the presence of a strong electron-withdrawing group can overcome these difficulties and a nucleophilic substitution then becomes possible. Hence, nitrobenzene when treated with strong base like NaOH in the presence of an oxidising agent such as KNO₃ gives *o*-nitrophenol.



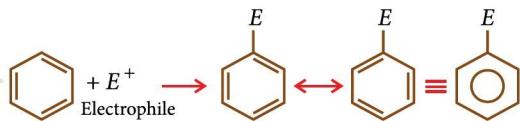
Mechanism

S_NAr reaction takes place by a two steps reaction. In the first step, nucleophile attacks the carbon bearing the leaving group. In the second step, the leaving group departs, re-establishing the aromaticity of the ring.



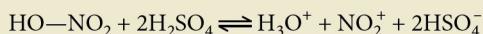
Electrophilic Substitution

An electrophilic substitution reaction is defined as a chemical reaction in which the hydrogen atom of benzene ring is replaced by an electrophile. These reactions are more common in aromatic compounds where π electrons are highly delocalised and an electrophile can readily attack this high electron density site.

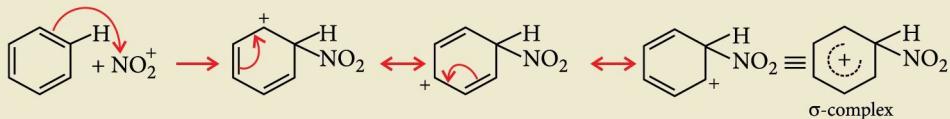


Mechanism

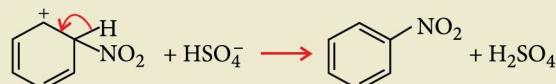
- (i) Generation of electrophile (attacking species) :



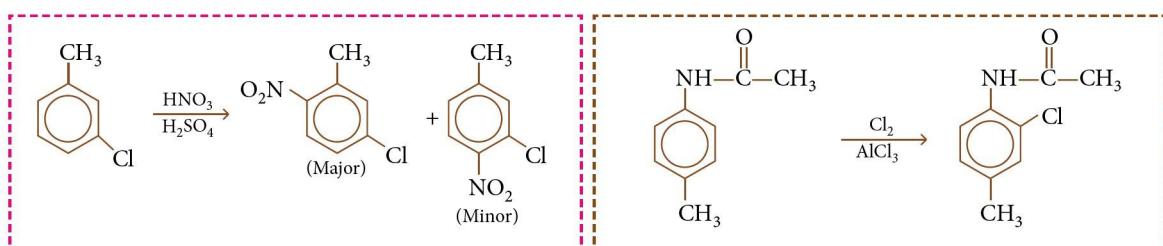
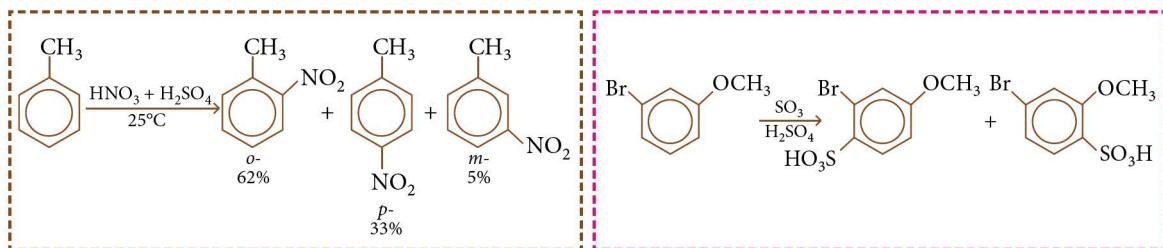
- (ii) Attack of electrophile to give a resonance stabilised σ -complex.



- (iii) Loss of proton to give the final substitution product.



Examples of electrophilic aromatic substitution reactions





for

NEET/JEE

CLASS-XI

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) 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.

Unit 2 Structure of Atom | Chemical Bonding and Molecular Structure

STRUCTURE OF ATOM

ATOM

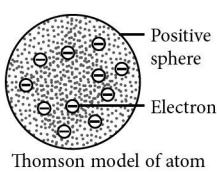
The word atom is a Greek word meaning indivisible. According to Dalton's atomic theory, atom is the smallest indivisible part of matter which takes part in chemical reactions. In 1833, Michael Faraday showed that there is a relationship between matter and electricity. The discovery of electrons, protons and neutrons discarded the indivisible nature of atom proposed by John Dalton.

Sub-atomic Particles

	Electron (e^-)	Proton (p)	Neutron (n)
Position	Moves around the nucleus	Constituent of nucleus	Constituent of nucleus
Charge	-1.6×10^{-19} C	$+1.6 \times 10^{-19}$ C	Neutral
Absolute mass (kg)	9.1×10^{-31}	1.67×10^{-27}	1.67×10^{-27}
Relative mass	1/1836	1	1
Discovery	J. J. Thomson	E. Goldstein	J. Chadwick

THOMSON MODEL OF ATOM (The Raisin Pudding Model)

- J. J. Thomson (1898) suggested that atom is a sphere (pudding) of positive charge with a number of electrons (raisins) distributed within the sphere, sufficient to neutralise the positive charge.
- The stability of the atom was explained as a result of the balance between the repulsive forces between the electrons and their attraction towards the centre of the positive sphere.



Thomson model of atom

- Although the model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments.

RUTHERFORD'S ATOMIC MODEL (NUCLEAR MODEL)

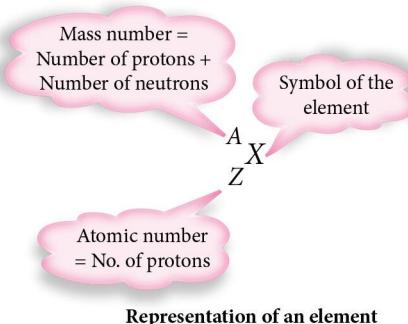
- Rutherford explained the structure of atom on the basis of his scattering experiment in which thin foil of metals like gold, silver, platinum, etc. was bombarded with fast moving α -particles.
- Various postulates of this model are**
 - Atom is spherical and consists of two parts, nucleus and extranuclear part.
 - Nucleus is very small in size. It is a positively charged, highly dense central core in which entire mass of the atom is concentrated.
 - Extranuclear part is an empty space around the nucleus where electrons are revolving in a circular orbit with very high speed. This nuclear model is comparable to our solar system in which planets are revolving around the sun. This model however, fails to explain the stability of atom and line spectrum of hydrogen.
 - Electrons and the nucleus are held together by electrostatic forces of attraction.
- Drawbacks of Rutherford's model of atom**
 - According to Rutherford's model of atom, electrons which are negatively charged particles revolve around the nucleus in fixed orbits. Thus, the electrons undergo acceleration. According to electromagnetic theory of Maxwell, a charged particle undergoing acceleration should emit electromagnetic radiations. Thus, an electron in an orbit should emit radiation. Thus, the orbit should shrink. But this does not happen.

- The model does not give any information about how electrons are distributed around nucleus and what are the energies of these electrons.

ATOMIC NUMBER AND MASS NUMBER

Atomic number : The positive charge of the nucleus is due to protons and each proton carries one unit positive charge, the atomic number of an element is equal to the number of protons in the nucleus of its atom.

In an atom, to keep the electrical neutrality the number of protons should be equal to the number of electrons. Hence, Atomic number (Z) = Number of protons = Number of electrons (in a neutral atom)



Mass number : Total number of protons and neutrons in the nucleus is called as mass number of the atom.

Mass number (A) = Number of protons (Z) + Number of neutrons (n)

Isobars and Isotopes

Isotopes : Isotopes are defined as the different atoms of the same element with same atomic numbers but different mass numbers. They have same number of protons but different number of neutrons. Isotopes of a given element show same chemical properties since the chemical behaviour of the atoms are influenced by the number of electrons, which are determined by number of protons in the nucleus. They show different physical properties as the physical properties depend on the mass which varies from one another, e.g., hydrogen has three isotopes; ${}^1_1\text{H}$, ${}^2_1\text{H}$ and ${}^3_1\text{H}$.

Isobars : Isobars are the atoms of different elements with same mass number but different atomic numbers. They have different number of neutrons and different number of protons but equal the sum of number of protons and neutrons inside the nucleus of an atom. The isobars have different physical and chemical properties ${}^{40}_{19}\text{K}$ and ${}^{40}_{20}\text{Ca}$.

- Isotones :** Nuclei having same number of neutrons are known as isotones of each other, e.g., ${}^{14}_6\text{C}$, ${}^{15}_7\text{N}$ and ${}^{16}_8\text{O}$.
- Isodiaphers :** Isodiaphers are the chemical species having same isotopic number. (Isotopic Number = Number of neutrons – Number of protons).
- Isoelectronic species :** Isoelectronic species are the chemical species having same number of electrons. e.g., O^{2-} , F^- , Na^+ , Mg^{2+} , etc.

DEVELOPMENTS LEADING TO THE BOHR'S MODEL OF ATOM

Wave Nature of Electromagnetic Radiations (Maxwell's Wave Theory)

Energy is emitted continuously from any source in the form of radiations travelling in the form of waves and are associated with electric and magnetic fields perpendicular to each other and to the direction of propagation. These waves are called **electromagnetic waves** or **electromagnetic radiations**.

- Characteristic properties of electromagnetic waves :**
 - Frequency (v) :** Number of waves that pass a given point in one second is called frequency and its SI unit is hertz or s^{-1} .
 - Wavelength (λ) :** It is the distance between any two consecutive crests or troughs. SI unit of wavelength is metre but is expressed in \AA (10^{-10} m), pm (10^{-12} m) or nm (10^{-9} m).
 - Velocity (c) :** It is the linear distance travelled by a wave in one second. In vacuum, all types of electromagnetic waves travel with same speed i.e., $3.0 \times 10^8 \text{ m s}^{-1}$ (speed of light).
 - Wave number (\bar{v}) :** It is defined as the number of wavelengths per unit length and its unit is m^{-1} . Its commonly used unit is cm^{-1} .
 - Amplitude :** The height of the crest or depth of the trough of a wave is called amplitude. It determines the intensity or brightness of the beam of light.
 - Relation between frequency, wavelength and velocity :** $c = v\lambda$ or $v = \frac{c}{\lambda}$
 - Relation between wave number and wavelength :** $\bar{v} = \frac{1}{\lambda}$
- Electromagnetic spectrum :** It is the arrangement of various types of electromagnetic radiations in order of their increasing wavelength or decreasing frequency.

- **Black body radiation** : The ideal body, which emits and absorbs all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation.
- **Planck's quantum theory** : Atoms and molecules can emit (or absorb) energy only in discrete quantities and not in a continuous manner. The smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation is called **quantum** and the energy associated with a quantum is proportional to its frequency i.e., $E = h\nu$, where h is Planck's constant having value equal to 6.626×10^{-34} J s.

The total amount of energy emitted or absorbed by a body in the form of small packets of energy are called **quanta** i.e.; $E = nh\nu$ where n is any integer. e.g., $E = 0, h\nu, 2h\nu, 3h\nu, \dots nh\nu \dots$

- **Photoelectric effect** : The phenomenon of ejection of electrons when certain metals (K, Rb, Cs etc.) are exposed to a beam of light having certain minimum frequency (threshold frequency, ν_0) is called photoelectric effect.

- **Kinetic energy of ejected electron** is given as :
Total energy – Threshold energy;

$$\text{K.E.} = \frac{1}{2} m_e v^2 = h\nu - h\nu_0$$

- $h\nu_0$ is called **work function** or threshold energy (minimum energy required to eject the electron).

- **Dual nature of electromagnetic radiation** : Light behaves either as a **wave** or as a stream of **particles**. When radiation interacts with matter, it displays particle like properties and when it propagates, it displays wave like properties.
- de Broglie wavelength of particles,

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

where, mv = momentum

- **Spectrum** : It is the combination of lights of different wavelengths analysed through a prism.
 - **Emission spectra** : When an excited electron returns back from higher energy level to ground state, it emits energy in the form of radiations. The spectrum produced is known as **emission spectrum**.
 - **Absorption spectra** : When white light from a source is first passed through a solution of a chemical substance, then radiation of a

particular wavelength is absorbed. Now if the light coming out from the solution is analysed, we get some dark lines (dark band) in the otherwise continuous spectrum, corresponding to the absorbed wavelength these dark lines appear at the same place where coloured lines appeared in the emission spectrum of the same substance.

The line spectrum results from the emission of radiations from atoms of the elements and thus called as atomic spectrum whereas molecules give band spectrum known as molecular spectrum

Hydrogen Spectrum

When an electric discharge is passed through hydrogen gas taken in a discharge tube at low pressure, some radiations are emitted. These radiations on spectroscopic analysis give emission spectrum of hydrogen.

Though a large number of lines appear in the hydrogen spectrum, their wavelengths can be measured by calculating their wave number by **Rydberg formula** i.e.,

$$\bar{\nu} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where R_H is a constant known as Rydberg constant.

$$R_H = 109677 \text{ cm}^{-1}$$

n_1 and n_2 are the electronic levels involved in transition

BOHR'S ATOMIC MODEL

The various postulates of the model are as follows :

- An atom consists of highly dense positively charged nucleus at the centre and electrons revolve around nucleus in circular orbits.
- Angular momentum of an electron in an atom is quantized.

$$mv = n \frac{h}{2\pi}$$

where, m = mass of electron, v = velocity of electron
 r = radius of orbit, n = number of orbit in which electron is present.

- The force of attraction is balanced by centrifugal forces, i.e.,

$$\text{Centrifugal force} = \frac{mv^2}{r}$$

$$\text{Force of attraction} = \frac{kZe^2}{r^2} \quad \text{or} \quad \frac{mv^2}{r} = \frac{kZe^2}{r^2}$$

$$\frac{mv^2}{r} = \frac{kZe^2}{r^2}$$

- Orbits in which electrons are revolving have fixed value of energy. These orbits are called **energy levels** or **stationary states**. As long as electrons are revolving in these orbits, they neither lose nor gain energy and hence this explains the stability of atom. The energy of a stationary state of hydrogen atom is

given as $E_n = -\frac{2\pi^2 me^4}{n^2 h^2}$ where n is the n^{th} energy level.

Putting the values of m and e in the above equation.

$$E_n = -\frac{21.8 \times 10^{-19}}{n^2} \text{ J/atom}$$

or $E_n = -\frac{13.6}{n^2} \text{ eV/atom}$ or $E_n = -\frac{1312}{n^2} \text{ kJ/mole}$

- Lowest energy state of electrons in an atom is the most stable state and is known as **ground state** or normal state. Electrons keep on revolving in this state without absorption or emission of energy.
- Absorption or emission of energy takes place during the transition of electron from lower to higher energy level or vice-versa respectively. Energy absorbed or released in an electronic transition is given as :

$$\Delta E = E_2 - E_1$$

where, ΔE is energy absorbed or emitted.

E_2 is energy at final state.

E_1 is energy at initial state of transition.

Radius of Bohr's Orbit

The radius of the orbit of an electron in a hydrogen-like atom is given by the formula:

$$r_n = \frac{0.529 \times n^2}{Z} \text{ Å} \quad \text{i.e., } r \propto n^2$$

Velocity of an Electron in an Orbit

Velocity with which an electron is revolving in an orbit is given by the formula:

$$v = \frac{2\pi e^2 Z}{nh} = \frac{2.19 \times 10^6 Z}{n} \text{ m/s}$$

Energy of Electron in an Orbit

From Bohr's theory, it has been calculated that energy of an electron in n^{th} orbit of a unielectron system is :

$$E_n = -\frac{2\pi^2 me^4 k^2}{n^2 h^2} Z^2$$

Substituting the values of π , m , e , k and h , we get,

$$E_n = -\frac{13.6}{n^2} Z^2 \text{ eV atom}^{-1}$$

$$= -\frac{2.179 \times 10^{-18}}{n^2} Z^2 \text{ J atom}^{-1} = -\frac{1312}{n^2} Z^2 \text{ kJ mol}^{-1}$$

where, Z is the atomic number.

It is obvious that $E \propto \frac{1}{n^2}$ i.e., negative energy of electron decreases with higher energy levels.

Hence, it can be shown that net energy of electron increases as it moves away from the nucleus (i.e., at higher energy levels) and reaches a value of zero at infinite distance from the nucleus. Although energy of electron increases with increase in the value of n , yet the difference of energy between successive orbits decreases. Thus,

$$E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > E_5 - E_4 \text{ and so on.}$$

If energy associated with n^{th} level of H-atom = E_n , the energy associated with n^{th} level of H-like one electron species (E'_n) is $E'_n = E_n Z^2$

Number of waves made by a Bohr electron in n^{th} orbit
Number of waves in any orbit

$$= \frac{\text{Circumference of that orbit}}{\text{Wavelength}}$$

$$= \frac{2\pi r}{\lambda} = \frac{2\pi r}{(h/mv)} = \frac{2\pi}{h} (mv) = \frac{2\pi}{h} \frac{nh}{2\pi} = n$$

Thus, number of waves in n^{th} orbit = n

Advantages of Bohr's Theory

- It explains the stability of atom.
- Line spectrum of hydrogen can be explained with Bohr's theory.
- Using the concept of Bohr's theory, radius of various orbits, velocity of electron and energy of electron in various orbits of hydrogen-like species can be calculated.

Drawbacks of Bohr's Theory

- Bohr's model does not explain the spectrum of multielectron atoms. It can only explain the spectrum of single electron species like H-atom, He^+ , Li^{2+} , Be^{3+} , etc.
- It does not explain the splitting of spectral lines under the influence of magnetic field (**Zeeman effect**) and in the electric field (**Stark effect**).
- Bohr's theory does not justify the principle of quantization of angular momentum.
- Bohr's Model fails to explain the de-Broglie concept of dual character and Heisenberg's principle of uncertainty.

- It could not explain the ability of atoms to form molecules by chemical bonds.

QUANTUM OR WAVE MECHANICAL MODEL OF ATOM

- Quantum mechanics developed by Erwin Schrodinger is based on the wave motion associated with the particles.
- Schrodinger wave equation :

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

QUANTUM NUMBERS

A set of four numbers which gives complete information about an electron in an atom.

Quantum number	Values	Information conveyed
Principal quantum number (n)	Any integer value i.e., 1, 2, 3, 4, etc.	Main shell of the electron. Approximate distance from the nucleus. Energy of shell. Maximum number of electrons present in the shell ($2n^2$). Explains the main lines of spectrum.
Azimuthal quantum number (l)	For a particular value of n , $l = 0$ to $n - 1$ $l = 0$, s -subshell $l = 1$, p -subshell $l = 2$, d -subshell $l = 3$, f -subshell	No. of subshells present in the main shell. Relative energies of the subshells. Shapes of orbitals. Explains the fine structure of the line spectrum.
Magnetic quantum number (m_l)	For a particular value of l , $m_l = -l$ to $+l$ including zero.	No. of orbitals present in any subshell. Explains the splitting of lines in a magnetic field.
Spin quantum number (m_s)	$+\frac{1}{2}$, $-\frac{1}{2}$	Direction of electron spin (clockwise or anticlockwise). Explains the magnetic properties of substances.

Filling of Orbitals in an Atom

The filling up of electrons in different orbitals is based on the following rules :

- Aufbau principle :** Orbitals are filled in the order of increasing energy. Lower the $(n + l)$ value, lower is the energy and if two orbitals have same $(n + l)$ value, orbital with lower value of n has lower energy. In the ground state of the atoms, the orbitals are filled in order of their increasing energies.
 $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s \dots$
- Pauli's exclusion principle :** No two electrons in an atom can have same set of four quantum numbers.

- The wave function ψ for an electron in an atom has no physical significance as such but ψ^2 gives the intensity of electron wave at that point or the probability of finding the electron at that point.
- An atomic orbital may be defined as the three dimensional space around the nucleus where the probability of finding an electron is maximum (upto 90-95%).

Nodes of Different Orbitals

- For a hydrogen atom of principal quantum number n , there are :
 - $(n - l - 1)$ radial nodes,
 - l angular nodes,
 - $(n - 1)$ total nodes.

CHEMICAL BONDING AND MOLECULAR STRUCTURE

- A **chemical bond** is the attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species.
- Two factors due to which atoms interact with each other are :

- Decrease in energy due to net attractive forces which are greater than repulsive forces.
- The tendency to achieve noble gas configurations.

KÖSSEL–LEWIS APPROACH TO CHEMICAL BONDING

- Atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to complete their octet or duplet. This is known as **octet rule**.
- There are two ways by which the atoms can acquire the stable inert gas configuration.
 - By complete transference of one or more electrons from one atom to another. This process is referred to as **electrovalency** and the chemical bond formed is termed as **electrovalent bond** or **ionic bond**.
 - By sharing of electrons. This can occur in two ways as follows :
 - When the shared electrons are contributed by the two combining atoms equally, the bond formed is called **covalent bond**.
 - When two atoms share one electron pair, they are said to be joined by a **single bond**.
 - If two atoms share two pairs of electrons, they are said to be joined by a **double bond**.
 - When combining atoms share three electron pairs, they are said to be joined by a **triple bond**.
 - When these electrons are contributed entirely by one of the atoms but shared by both, the bond formed is known as a **coordinate bond**, also called **dative bond**.
This bond is represented by an arrow (\longrightarrow).



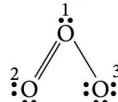
- The atom which contributes electron pair is called the donor while the atom which accepts it, is called the acceptor.

Fajan's rule : No bond is 100% ionic or covalent. Ionic bonds have partial covalent character. According to Fajan's, covalent character in ionic bonds increases with:

- smaller size of cation,
- larger size of anion
- greater charge on cation/anion.

Lewis Dot Structures

- The structures in which valence electrons are represented by 'dots' around the atom are called Lewis dot structures.
- Formal charge = Total number of valence electrons in the free atom
 - Total number of non-bonding (lone pair) electrons
 - $\frac{1}{2} \times$ Total number of bonding (shared) electrons
- The Lewis structure of O_3 may be drawn as :



The atoms have been numbered as 1, 2 and 3. The formal charge on :

The central O atom marked 1 = $6 - 2 - \frac{1}{2}(6) = +1$

The end O atom marked 2 = $6 - 4 - \frac{1}{2}(4) = 0$

The end O atom marked 3 = $6 - 6 - \frac{1}{2}(2) = -1$

Exceptions to Octet Rule

There are some compounds which violate the octet rule and still quite stable.

- Electron deficient compounds** : These are the stable compounds which have electrons less than noble gas configuration in their octet. For example, hydrides of boron BH_3 , B_2H_6 ; halides of boron BCl_3 , BF_3 ; AlCl_3 , BeCl_2 , etc.
- Electron rich compounds** : These are the stable compounds which have electrons more than noble gas configuration in their octet. For example, PCl_5 , SF_6 , IF_7 , etc.

BOND PARAMETERS

Bond Length

- Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond length is expressed in Angstrom ($1 \text{ \AA} = 10^{-10} \text{ m}$) or in picometer ($1 \text{ pm} = 10^{-12} \text{ m}$).
- The **covalent radius** is half of the distance between two similar atoms joined by a covalent bond in the same molecule.
- The **van der Waals radius** is half the distance between centres of nuclei of two non-bonded atoms of adjacent molecules in solid state.

Bond Angle

- If a molecular is made up of three or more atoms, the average angle between bonded orbitals is known as bond angle.

- Bond angle gives an idea of the distribution of orbitals in three-dimensional space around the central atom.

Bond Enthalpy

- It is the amount of energy required to break one mole of bond of a particular type and separate the bonded atoms in the gaseous state. It is also called as **bond dissociation energy**. It is expressed in kJ mol^{-1} .
- In a polyatomic molecule, a particular type of bond (e.g., 4 C—H bonds in CH_4) does not possess the same bond energy due to change in chemical environment, therefore the bond energies taken are usually the average values. For example, in H_2O , first O—H bond energy = 502 kJ mol^{-1} and second O—H bond energy = 427 kJ mol^{-1} .

Hence, average bond dissociation energy =

$$\frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$$

Dipole Moment

The polarity of a molecule is indicated in terms of dipole moment (μ). The dipole moment is defined as the product of the distance separating charges of equal magnitude and opposite sign (d), with the magnitude of the charge (q). The distance between the positive and negative centres is called the bond length. Thus, $\mu = q \times d$.

The charge q is in the order of 10^{-10} esu and d is in the order of 10^{-8} cm, hence, μ is in the order of 10^{-18} esu cm. Dipole moment is measured in ‘Debye’ unit (D).

$1\text{D} = 10^{-18} \text{ esu cm} = 3.335 \times 10^{-30} \text{ coulomb metre}$

Dipole moment is a vector quantity, i.e., it has both magnitude as well as direction.

Presence of dipole moment is indicated by the crossed arrow (\longleftrightarrow) on Lewis structure of the molecule, the cross is on positive and arrow head is on negative end.

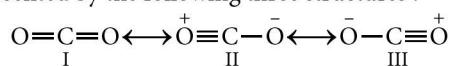
Resonance

It has been observed that in case of certain molecules, a single Lewis structure cannot explain all the properties of the molecule. The molecule is then supposed to have more than one structures, each of which can explain most of the properties of the molecules, but none of which is able to explain all the properties of the molecule.

According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule, two or more alternate valence bond structures with similar

energy, positions of nuclei, bonding and non-bonding pairs of electrons can be written for a molecule. The actual structure is said to be a resonance or mesomeric hybrid of all these contributing structures and the different individual structures are called resonating structures or canonical forms.

For example, carbon dioxide molecule can be represented by the following three structures :



The calculated values of bond length between carbon and oxygen in $\text{C}=\text{O}$ and $\text{C}\equiv\text{O}$ are 1.22 \AA and 1.10 \AA , respectively but the observed bond length between carbon and oxygen in carbon dioxide is 1.15 \AA .

HYBRIDISATION

- Linus Pauling in 1931 proposed that the atomic orbitals of similar energies in the valence shell of the same atom combine with each other resulting in more stable set of orbitals called **hybrid orbitals**. This process of mixing of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy is known as hybridisation.
- Hybridisation : $H = \frac{1}{2}(V + M - C + A)$

where, H = number of orbitals involved in hybridisation viz. 2, 3, 4, 5, 6 and 7, hence nature of hybridisation will be sp , sp^2 , sp^3 , sp^3d , sp^3d^2 , sp^3d^3 respectively.

V = number of electrons in valence shell of the central atom; M = number of monovalent atom; C = charge on cation; A = charge on anion

VSEPR THEORY AND MOLECULAR SHAPES

VSEPR theory was given by Sidgwick and Powell in 1940. In a molecule, the central atom is surrounded by shared pair of electrons (bond pairs) as well as non-bonding electrons (lone pairs). The electron pairs surrounding the central atom repel each other and move away from one another to occupy the most appropriate position in such a way that there are no further repulsions between them and molecule is in the state of minimum energy and maximum stability. The order of repulsion between electron pairs is as follows :

lone pair-lone pair > lone pair-bond pair > bond pair-bond pair.

- Hybridisation and structures of molecules having bond pairs only :

Type of hybridisation	No. of hybrid orbitals	Shape of molecule	Bond angle	Examples
sp	2	Linear	180°	$\text{BeCl}_2, \text{BeF}_2, \text{CO}_2, \text{CS}_2, \text{C}_2\text{H}_2, \text{N}_2\text{O}, [\text{Ag}(\text{CN})_2]^-$, $\text{HgCl}_2, \text{HCN}$
sp^2	3	Triangular planar	120°	$\text{BF}_3, \text{BCl}_3, \text{C}_2\text{H}_4, \text{NO}_3^-, \text{CO}_3^{2-}, \text{SO}_3$
sp^3	4	Tetrahedral	109.5°	$\text{CH}_4, \text{CCl}_4, \text{SnCl}_4, \text{SiF}_4, \text{NH}_4^+, \text{SO}_4^{2-}$
dsp^2	4	Square planar	90°	$[\text{PtCl}_4]^{2-}, [\text{Ni}(\text{CN})_4]^{2-}$
dsp^3 or sp^3d	5	Trigonal bipyramidal	120° and 90°	$\text{PCl}_5, \text{PF}_5, [\text{Fe}(\text{CO})_5]$
d^2sp^3 or sp^3d^2	6	Octahedral	90°	$\text{SF}_6, \text{UF}_6, \text{TeF}_6, [\text{CrF}_6]^{3-}, [\text{Co}(\text{NH}_3)_6]^{3+}$
d^3sp^3 or sp^3d^3	7	Pentagonal bipyramidal	72° and 90°	IF_7

- Hybridisation and structures of molecules having lone pair(s) :

Types of molecules	No. of bond pair(s)	No. of lone pair(s)	Hybridisation	Bond angle	Expected geometry	Actual geometry	Examples
AX_2	2	1	sp^2	$<120^\circ$	Trigonal planar	V-shaped or Bent	$\text{SO}_2, \text{SnCl}_2, \text{PbCl}_2, \text{NO}_2^+, \text{O}_3$
AX_2	2	2	sp^3	$<109^\circ 28'$	Tetrahedral	V-shaped or Bent	$\text{H}_2\text{O}, \text{H}_2\text{S}, \text{SCl}_2, \text{OF}_2, \text{Cl}_2\text{O}, \text{ClO}_2^-$
AX_2	2	3	sp^3d	180°	Trigonal bipyramidal	Linear	$\text{XeF}_2, \text{I}_3^-, \text{ICl}_2^-$
AX_3	3	2	sp^3d	90°	Trigonal bipyramidal	T-shaped	$\text{ClF}_3, \text{IF}_3, \text{BrF}_3, \text{XeOF}_2$
AX_3	3	1	sp^3	$<109^\circ 28'$	Tetrahedral	Pyramidal	$\text{NH}_3, \text{PH}_3, \text{PCl}_3, \text{BiCl}_3, \text{AsCl}_3, \text{XeO}_3, \text{ClO}_3^-$
AX_4	4	1	sp^3d	120° 90°	Trigonal bipyramidal	See saw or Distorted tetrahedron	$\text{SF}_4, \text{SCl}_4, \text{TeCl}_4, \text{XeO}_2\text{F}_2$
AX_4	4	2	sp^3d^2	—	Octahedral	Square planar	$\text{XeF}_4, \text{ICl}_4^-$
AX_5	5	1	sp^3d^2	$<90^\circ$	Octahedral	Square pyramidal	$\text{IF}_5, \text{BrF}_5, \text{SbF}_5^{2-}$
AX_6	6	1	sp^3d^3	—	Pentagonal bipyramidal	Distorted octahedral	XeF_6

VALENCE BOND THEORY

- This theory was introduced by Heitler and London (1927) and developed further by Pauling and others. Its main postulates are :
 - Bond is formed due to interaction of valence

electrons. The core electrons do not participate in bond formation.

- During bond formation, only valence electrons lose their identity.
- Bond formation is accompanied by release of energy and this accounts for the stability of the bond.

- The molecule has minimum energy at the equilibrium distance known as the intermolecular distance. Larger the decrease in energy, stronger will be the bond formed.

MOLECULAR ORBITAL THEORY

- Molecular orbitals are formed by the addition or subtraction of wave functions of the atomic orbitals.
- Addition of wave functions during overlap of atomic orbitals leads to formation of bonding orbitals with lower energy levels, they can be σ or π .
- Subtraction of wave functions during overlap of atomic orbitals leads to formation of anti-bonding orbitals with higher energy levels, written as σ^* or π^* .
- Filling of electrons in molecular orbitals takes place in accordance with Aufbau's principle, Hund's rule and Pauli's exclusion principle.

- Energy order for molecular orbitals upto N₂ is
 $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$
- Energy order for molecules beyond N₂ is
 $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi^* 2p_y < \sigma^* 2p_z$

Bond Order

- The number of covalent bonds formed in a molecule is called its bond order. Mathematically, it is defined as half of the difference between the number of bonding and antibonding electrons.
- Bond order (B.O.) = $\frac{1}{2} (N_b - N_a)$
- Isoelectronic species have same bond order.

$$\text{Bond order} \propto \text{stability} \propto \frac{1}{\text{bond length}}$$



WRAP it up!

MCQs TYPE QUESTIONS

- For Balmer series in the spectrum of atomic hydrogen, the wave number of each line is given by $\bar{v} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$, where R_H is a constant and n₁ and n₂ are integers. Which of the following statements are correct?
 - As wavelength decreases, the lines in the series converge.
 - The integer n₁ is equal to 2.
 - The ionization energy of hydrogen can be calculated from the wave number of these lines.
 - The line of longest wavelength corresponds to n₂ = 3.
 - I, II and III only
 - II, III and IV only
 - I, II and IV only
 - II and IV only
- Select the pair that has the same bond order with diamagnetic and paramagnetic properties respectively.
 - F₂ and O₂
 - N₂ and O₂²⁻
 - Li₂ and B₂
 - B₂ and O₂
- The electrons identified by quantum numbers n and l:

(1) n = 4, l = 1	(2) n = 4, l = 0
(3) n = 3, l = 2	(4) n = 3, l = 1

 can be placed in order of increasing energy as
 - (4) < (2) < (3) < (1)
 - (2) < (4) < (1) < (3)
 - (1) < (3) < (2) < (4)
 - (3) < (4) < (2) < (1)
- In which of the following pairs of molecules/ions, both the species are not likely to exist?
 - H₂⁻, He₂²⁺
 - H₂⁺, He₂²⁻
 - H₂⁻, He₂²⁻
 - H₂²⁺, He₂
- Maximum number of electrons in a subshell of an atom is determined by the following
 - 2l + 1
 - 4l - 2
 - 2n²
 - 4l + 2
- Among the following, the pair in which the two species are not isostructural is
 - SiF₄ and SF₄
 - IO₃⁻ and XeO₃
 - BH₄⁻ and NH₄⁺
 - PF₆⁻ and SF₆
- The velocity of the electron in the first Bohr orbit of H-atoms is 2.2×10^8 cm/sec. The velocity of the electron in the third Bohr-orbit of Li²⁺ (atomic number = 3) is
 - 19.8×10^8 cm/sec
 - 6.6×10^8 cm/sec
 - 4.4×10^8 cm/sec
 - 2.2×10^8 cm/sec

- 8.** Dipole moment is shown by
 (a) 1,4-dichlorobenzene
 (b) *cis*-1,2-dichloroethene
 (c) *trans*-1,2-dichloroethene
 (d) *trans*-2,3-dichloro-2-butene.
- 9.** Light of wavelength λ shines on a metal surface with intensity x and the metal emits y electrons per second of average energy, z . What will happen to y and z if x is doubled?
 (a) y will be doubled and z will become half
 (b) y will remain same and z will be doubled
 (c) both y and z will be doubled
 (d) y will be doubled but z will remain same.
- 10.** Of the following sets which does not contain isoelectronic species?
 (a) PO_4^{3-} , SO_4^{2-} , ClO_4^- (b) CN^- , N_2 , C_2^{2-}
 (c) SO_3^{2-} , CO_3^{2-} , NO_3^- (d) BO_3^{3-} , CO_3^{2-} , NO_3^-
- 11.** The frequency of the radiation emitted when the electron falls from $n = 4$ to $n = 1$ in a hydrogen atom will be (Given ionization energy of H = 2.18×10^{-18} J atom $^{-1}$ and $h = 6.625 \times 10^{-34}$ J s)
 (a) 1.54×10^{15} s $^{-1}$ (b) 1.03×10^{15} J s $^{-1}$
 (c) 3.08×10^{15} s $^{-1}$ (d) 2.0×10^{15} s $^{-1}$.
- 12.** Among LiCl , BeCl_2 , BCl_3 and CCl_4 , the covalent bond character varies as
 (a) $\text{LiCl} < \text{BeCl}_2 > \text{BCl}_3 > \text{CCl}_4$
 (b) $\text{BCl}_3 > \text{BeCl}_2 > \text{CCl}_4 > \text{LiCl}$
 (c) $\text{LiCl} < \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$
 (d) $\text{LiCl} > \text{BeCl}_2 > \text{BCl}_3 > \text{CCl}_4$
- 13.** The statement that is not correct is
 (a) angular quantum number signifies the shape of the orbital
 (b) energies of stationary states in hydrogen like atoms is inversely proportional to the square of the principal quantum number
 (c) total number of nodes for $3s$ orbital is three
 (d) the radius of the first orbit of He^+ is half that of the first orbit of hydrogen atom.
- 14.** Match column I with column II and select the correct option.
- | Column I | | Column II | |
|----------|------------------------|-----------|------------------------|
| P. | PCl_5 | 1. | Linear |
| Q. | IF_7 | 2. | Pyramidal |
| R. | H_3O^+ | 3. | Trigonal bipyramidal |
| S. | ClO_2^- | 4. | Tetrahedral |
| T. | NH_4^+ | 5. | Pentagonal bipyramidal |
| | | 6. | V-shaped |
- 15.** Match column I with column II and select the correct option from the given codes.
- | Column I | | Column II | |
|----------|---|-----------|-----------------|
| P. | Electronic configuration of Fe in FeCl_3 | 1. | [Ar] $3d^8$ |
| Q. | Electronic configuration of Ni in NiCl_2 | 2. | [Ar] $3d^{10}$ |
| R. | Electronic configuration of O in OF_2 | 3. | [Ar] $3d^5$ |
| S. | Electronic configuration of Cu in CuCl | 4. | [He] $2s^22p^2$ |
- (a) P-2, Q-4, R-1, S-3 (b) P-3, Q-1, R-4, S-2
 (c) P-1, Q-3, R-4, S-2 (d) P-4, Q-2, R-1, S-3
- 16.** Some of the properties of the two species, NO_3^- and H_3O^+ are described below. Which one of them is correct?
 (a) Dissimilar in hybridization for the central atom with different structures
 (b) Isostructural with same hybridization for the central atom
 (c) Isostructural with different hybridization for the central atom
 (d) Similar in hybridization for the central atom with different structures
- 17.** The boiling point of *p*-nitrophenol is higher than that of *o*-nitrophenol because
 (a) NO_2 group at *p*-position behaves in a different way from that at *o*-position
 (b) intramolecular hydrogen bonding exists in *p*-nitrophenol
 (c) there is intermolecular hydrogen bonding in *p*-nitrophenol
 (d) *p*-nitrophenol has a higher molecular weight than *o*-nitrophenol.
- 18.** **Assertion :** According to Bohr's theory, electrons move in circular orbits of fixed radius and energy.
Reason : Only those circular orbitals are allowed in which angular momentum is an integral multiple of $h/2\pi$.
 (a) Both assertion and reason are true and reason is the correct explanation of assertion.
 (b) Both assertion and reason are true but reason is not the correct explanation of assertion.

NUMERICAL VALUE TYPE QUESTIONS

21. The de Broglie wavelength of an electron in the 4th Bohr orbit is _____ $\times \pi a_0$.

22. The dipole moment of LiH is 1.964×10^{-29} C m and interatomic distance between Li and H in the molecule is 1.596 Å. The percentage of ionic character of the molecule is _____.

23. The difference between bond orders for O₂⁺ and C₂⁺ is _____.

24. The outer orbitals of C in ethene molecule can be considered to be hybridized to give three equivalent sp^2 orbitals. The sum of sigma (σ) and pi (π) bonds in ethene molecule is _____.

25. An electron transition in the hydrogen atom involves an energy change of 40.5 kcal per mole. The wavelength (in nm) associated with their transition is _____.

SOLUTIONS

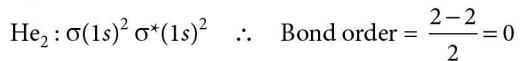
- | 1. (c) | Species | Bond order | Magnetic behaviour |
|----------|------------|------------|--------------------|
| 2. (c) : | F_2 | 1 | Diamagnetic |
| | O_2 | 2 | Paramagnetic |
| | N_2 | 3 | Diamagnetic |
| | O_2^{2-} | 1 | Diamagnetic |
| | Li_2 | 1 | Diamagnetic |
| | B_2 | 1 | Paramagnetic |

3. (a) : (1) $n = 4, l = 1 \Rightarrow 4p$
(2) $n = 4, l = 0 \Rightarrow 4s$ (3) $n = 3, l = 2 \Rightarrow 3d$

$$3. \text{ (a)}: (1) n = 4, l = 1 \Rightarrow 4p \\ (2) n = 4, l = 0 \Rightarrow 4s, (3) n = 3, l = 2 \Rightarrow 3d$$

- (4) $n = 3, l = 1 \Rightarrow 3p$
 Increasing order of energy is $3p < 4s < 3d < 4p$ i.e.,
 $(4) < (2) < (3) < (1)$
 Alternatively, the order of increasing energies of the various orbitals can be calculated on the basis of $(n + l)$ rule. As per the rule, in a neutral isolated atom, the lower the value of $(n + l)$ for an orbital, lower is its energy. However if the two different types of orbitals have the same value of $(n + l)$, the orbitals with lower value of n has lower energy.

- 4. (d):** Species with zero bond order does not exist.



5. **(d):** For a given shell, l , the number of subshells, $m_l = (2l + 1)$
 Since each subshell can accommodate 2 electrons of opposite spin, so maximum number of electrons in a subshell = $2(2l + 1) = 4l + 2$.

6. (a)

$$\begin{aligned}
 \text{(d): } v &\propto \frac{Z}{n} \\
 v_1 &\propto \frac{Z_1}{n_1}; v_2 \propto \frac{Z_2}{n_2} & Z_1 = 1; & n_1 = 1 \\
 \frac{v_1}{v_2} &= \frac{Z_1}{n_1} \times \frac{n_2}{Z_2} = \frac{1}{1} \times \frac{3}{3} = 1 \\
 \frac{v_1}{v_2} &= 1 \Rightarrow v_1 = v_2 \Rightarrow v_2 = 2.2 \times 10^8 \text{ cm/s}
 \end{aligned}$$

8. (b)

9. (d)

$$10. (c) : \text{Number of electrons in } \text{SO}_3^{2-} = 16 + (3 \times 8) + 2 \\ = 42$$

Number of electrons in $\text{CO}_3^{2-} = 6 + (3 \times 8) + 2 = 32$

- ### Number of electrons in Ne^{+}

$$(c) : I.E. = E_{\infty} - E_1 = 0 - E_1$$

$$\text{Thus, } E_n = -\frac{2.18 \times 10^{-18}}{2} \text{ J mol}^{-1}$$

$$\Delta E = E_4 - E_1 = -2.18 \times 10^{-18} \left(\frac{1}{4^2} - \frac{1}{1^2} \right) = -2.044 \times 10^{-18} \text{ J atom}^{-1}$$

$$\Delta E = h\nu \quad \text{or, } \nu = \frac{\Delta E}{h} = \frac{2.044 \times 10^{-18} \text{ J}}{6.625 \times 10^{-34} \text{ Js}} = 3.085 \times 10^{15} \text{ s}^{-1}$$

12. (c)

- 13. (c) :** No. of nodes for any orbital = $n - l - 1$
 For $3s$ -orbital, $n = 3$ and $l = 0$

14. (d) : $\text{PCl}_5 \rightarrow sp^3d$ hybridisation \rightarrow Trigonal bipyramidal
 $\text{IF}_7 \rightarrow sp^3d^3$ hybridisation \rightarrow Pentagonal bipyramidal
 $\text{H}_3\text{O}^+ \rightarrow sp^3$ hybridisation \rightarrow Pyramidal
 $\text{ClO}_2^- \rightarrow sp^3$ hybridisation \rightarrow V-shaped
 $\text{NH}_4^+ \rightarrow sp^3$ hybridisation \rightarrow Tetrahedral

15. (b)

16. (a) : Hybridisation = $1/2(V + X - C + A)$
 Here, V = Number of valence electrons in central atom
 X = Number of monovalent atoms around the central atom
 C = Positive charge on cation
 A = Negative charge on anion

$$\text{In } \text{NO}_3^-, H = \frac{1}{2}(5+1) = 3 \quad (\text{sp}^2 \text{ hybridisation})$$

The structure of NO_3^- is trigonal planar

$$\text{In } \text{H}_3\text{O}^+, H = \frac{1}{2}(6+3-1) = 4 \quad (\text{sp}^3 \text{ hybridisation})$$

The structure of H_3O^+ is pyramidal.

17. (c)

18. (b)

19. (c) : Molecular orbital configuration of
 $\text{N}_2 \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2 \Rightarrow \text{diamagnetic}$

$$\text{Bond order} = \frac{10-4}{2} = 3$$

$$\text{N}_2^+ \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^1 \Rightarrow \text{paramagnetic}$$

$$\text{Bond order} = \frac{9-4}{2} = 2.5$$

$$\text{C}_2 \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \Rightarrow \text{diamagnetic}$$

$$\text{Bond order} = \frac{8-4}{2} = 2$$

$$\text{C}_2^+ \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^1 \Rightarrow \text{paramagnetic}$$

$$\text{Bond order} = \frac{7-4}{2} = 1.5$$

$$\text{NO} \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 \Rightarrow \text{paramagnetic}$$

$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

$$\text{NO}^+ \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \Rightarrow \text{diamagnetic}$$

$$\text{Bond order} = \frac{10-4}{2} = 3$$

$$\text{O}_2 \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \\ \pi^* 2p_x^1 = \pi^* 2p_y^1 \Rightarrow \text{paramagnetic}$$

$$\text{Bond order} = \frac{10-6}{2} = 2$$

$$\text{O}_2^+ \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 \\ \Rightarrow \text{paramagnetic}$$

$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

20. (c) : P in PCl_5 is sp^3d hybridised and I in IF_5 is sp^3d^3 hybridised.

$$21. (8) : 2\pi r = n\lambda \quad \therefore r = a_0 n^2 \\ \therefore 2\pi a_0 n^2 = n\lambda \Rightarrow \lambda = 2\pi a_0 n \Rightarrow 8\pi a_0 \\ (\because n = 4)$$

22. (77) : If the molecule was 100% ionic then

$$\mu_{\text{ionic}} = q \times d; q = 1.602 \times 10^{-19} \text{ C} \\ = (1.602 \times 10^{-19} \text{ C}) \times (1.596 \times 10^{-10} \text{ m}) \\ = 2.557 \times 10^{-29} \text{ C m}$$

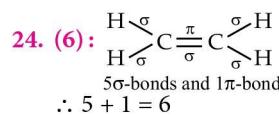
$$\mu_{\text{observed}} = 1.964 \times 10^{-29} \text{ C m} \\ \therefore \% \text{ ionic character} =$$

$$\frac{1.964 \times 10^{-29}}{2.557 \times 10^{-29}} \times 100 = 76.81\% \approx 77$$

$$23. (1) : \text{Bond order} = \frac{N_b - N_a}{2}$$

Species	No. of electrons	M.O. configuration	B.O.
O_2^+	15	$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, (\pi 2p_x^2 = \pi 2p_y^2), (\pi^* 2p_x^1 = \pi^* 2p_y^0)$	2.5
C_2^+	11	$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, (\pi 2p_x^2 = \pi 2p_y^1)$	1.5

$$\text{Difference} = 2.5 - 1.5 = 1$$



$$25. (706) : \Delta E = \frac{hc}{\lambda}$$

$$\text{Energy per H-atom} = \frac{40.5 \times 10^3 \times 4.184 \text{ J/mol}}{6.023 \times 10^{23}}$$

$$= 2.8134 \times 10^{-19} \text{ J} \quad (1 \text{ cal} = 4.184 \text{ J/mol})$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{2.8134 \times 10^{-19}}$$

$$= 7.065 \times 10^{-7} \text{ m} = 706.5 \times 10^{-9} \text{ m} = 706 \text{ nm}$$





CBSE warm-up!

CLASS-XI

Chapterwise practice questions for CBSE Exams as per the latest pattern and rationalised syllabus by CBSE for the academic session 2023-24.

Series-3

Classification of Elements and Periodicity in Properties | Chemical Bonding and Molecular Structure

Time Allowed : 3 hours
Maximum Marks : 70

General Instructions

Read the following instructions carefully.

- (a) There are 33 questions in this question paper with internal choice.
 - (b) SECTION-A consists of 16 multiple-choice questions carrying 1 mark each.
 - (c) SECTION-B consists of 5 short answer questions carrying 2 marks each.
 - (d) SECTION-C consists of 7 short answer questions carrying 3 marks each.
 - (e) SECTION-D consists of 2 case-based questions carrying 4 marks each.
 - (f) SECTION-E consists of 3 long answer questions carrying 5 marks each.
 - (g) All questions are compulsory.
 - (h) Use of log tables and calculators is not allowed.

SECTION-A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

- 1.** Which of the following statements is correct?

 - (a) X^- ion is larger in size than X atom.
 - (b) X^+ ion is larger in size than X atom.
 - (c) X^+ and X^- ions are equal in size.
 - (d) X^+ ion is larger in size than X^- ion.

2. The correct order of increasing ionic character?

 - (a) $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{BaCl}_2$
 - (b) $\text{BeCl}_2 < \text{MgCl}_2 < \text{BaCl}_2 < \text{CaCl}_2$
 - (c) $\text{BeCl}_2 < \text{BaCl}_2 < \text{MgCl}_2 < \text{CaCl}_2$
 - (d) $\text{BaCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$

3. Which of the following elements has highest electron affinity?

 - (a) Na
 - (b) K
 - (c) Cl
 - (d) F

4. Which of the following have similar values of electronegativity?

- 9.** The molecule having one unpaired electron is
 (a) NO (b) CO₂ (c) Li₂ (d) O₂
- 10.** The formal charge on central oxygen atom in ozone is
 (a) 0 (b) +2 (c) +1 (d) -1
- 11.** Among the elements B, Mg, Al and K, the correct order of increasing metallic character is
 (a) B < Al < Mg < K (b) B < Mg < Al < K
 (c) Mg < B < Al < K (d) Mg < Al < B < K
- 12.** The correct order of ionisation energy of C, N, O and F is
 (a) F < N < C < O (b) C < N < O < F
 (c) C < O < N < F (d) F < O < N < C
- 13.** Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Metallic character is highest at the extremely left side of the periodic table.
Reason (R) : Ionisation enthalpy decreases across a period.
 Select the most appropriate answer from the options given below :
 (a) Both A and R are true and R is the correct explanation of A.
 (b) Both A and R are true 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.
- 14.** Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Na₂O is a basic oxide whereas Cl₂O₇ is an acidic oxide.
Reason (R) : Elements on extreme left form basic oxides whereas elements on extreme right form acidic oxides.
 Select the most appropriate answer from the options given below :
 (a) Both A and R are true and R is the correct explanation of A.
 (b) Both A and R are true 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.
- 15.** Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : F₂ and O₂²⁻ have bond order 1 while N₂, CO and NO⁺ have bond order 3.
Reason (R) : Higher the bond order, higher is the stability of the molecule.

Select the most appropriate answer from the options given below :

- (a) Both A and R are true and R is the correct explanation of A.
 (b) Both A and R are true 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.

- 16.** Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion (A) : Dipole moment of NH₃ is greater than that of NF₃.

Reason (R) : Nitrogen is more electronegative than fluorine.

Select the most appropriate answer from the options given below :

- (a) Both A and R are true and R is the correct explanation of A.
 (b) Both A and R are true 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.

SECTION-B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

- 17.** Which of the following species will have the largest and the smallest size?

Mg, Mg²⁺, Al, Al³⁺

- 18.** Arrange the following in increasing order of the property indicated :

- (i) SiO₂, P₂O₅, SO₃ and Cl₂O₇ (acidic nature)
 (ii) C, N, O and F (2nd ionisation enthalpy)

- 19.** Draw the structures of XeF₄ and OSF₄ according to VSEPR theory, clearly indicating the state of hybridisation of the central atom and lone pair of electrons (if any) on the central atom.

OR

Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C₂H₄ and C₂H₂ molecules.

- 20.** The dipole moment of KCl is 3.336×10^{-29} C m. The interatomic distance between K⁺ and Cl⁻ in this molecule is 2.6×10^{-10} m. Calculate percentage ionic character of KCl.

- 21.** Two elements X and Y have atomic numbers 16 and 19 respectively.

- (i) Write down the electronic configurations of X and Y.
- (ii) Which element belongs to s-block?
- (iii) Which element belongs to p-block?

SECTION-C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. (a) First ionization energy of carbon atom is greater than that of boron whereas the reverse is true for second ionization energy. Explain.
 (b) Why alkali metals do not form dipositive ions?
23. Account for the following :
 - (i) Be in the second period of the periodic table has slightly higher first ionization enthalpy than B.
 - (ii) Electron gain enthalpy of atoms become more negative from left to right along a period in the periodic table.
24. (a) What is the significance of the term “isolated gaseous atom” while defining ionization enthalpy?
 (b) Na and Mg⁺ have the same number of electrons but removal of electron from Mg⁺ requires more energy. Give reason.
 (c) Elements in the same group have similar chemical properties. Give reason.

OR

Explain the following :

- (a) Electronegativity of elements increases on moving from left to right in the periodic table.
- (b) Ionisation enthalpy decreases in a group from top to bottom.
- (c) The metallic and non-metallic character vary on moving from left to right in a period.

25. Write the significance/applications of dipole moment.
26. Give the shapes of following covalent molecules using VSEPR theory:
 (i) PCl₅ (ii) ClF₃ (iii) XeF₄
27. What are the salient features of molecular orbital theory (MOT)?
28. Write the molecular orbital configuration of the following species : O₂, O₂⁺, O₂⁻, O₂²⁻. Arrange them in order of their decreasing stabilities.

SECTION-D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. When covalent bond is formed between two similar atoms, for example in H₂, O₂, Cl₂, N₂ or F₂, the shared pair of electrons is equally attracted by the two atoms. As a result, electron pair is situated exactly between the two identical nuclei. The bond so formed is called non-polar covalent bond. In case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond. As a result of polarisation, the molecule possesses the dipole moment.

Dipole moment = Electric charge × Distance of separation

$$\text{or } \mu = q \times d$$

Dipole moment is measured in ‘Debye’ unit (D). Non-polar diatomic molecules have zero dipole moment while for a polar diatomic molecule, the dipole moment of molecule is not equal to zero and depends on the dipole moment of the polar bond. Molecules with regular geometry have zero dipole moment while molecules with irregular geometry (having bond pair and lone pair) possess a definite dipole moment.

Answer the following questions :

- (a) Which of the following molecule/molecules will not have zero dipole moment? CO₂, H₂O, BeF₂, NH₃.

OR

A trigonal planar AX₃ molecule has a zero dipole moment although A—X bonds are polar. Why?

- (b) Which has a higher dipole moment CCl₄ or CH₃Cl?
- (c) Why dipole moment of CO₂ is zero while H₂O is polar though both are triatomic?

30. In 1913, Henry Moseley observed regularities in the characteristic X-ray spectra of the elements. He observed that a plot of $\sqrt{\nu}$ (where ν is the frequency of X-rays emitted) against atomic number (Z) gave a straight line and not the plot of $\sqrt{\nu}$ vs atomic weight. He thereby showed that the atomic number is a more fundamental property of an element than its atomic mass. Mendeleev’s periodic law was therefore accordingly modified. This is known as the modern periodic law and can be stated as : “The physical and chemical properties of elements are the periodic functions of their atomic numbers”. If the elements are arranged in

order of their increasing atomic number, after a regular interval, element with similar properties are repeated. In the long form of the periodic table there are seven horizontal rows called periods and eighteen vertical columns called groups.

Answer the following questions :

- (a) Where are the particular elements with similar physical and chemical properties placed in the periodic table?
- (b) Why argon (at. mass 39.94) has been placed before potassium (at. mass 39.10) in the modern periodic table?
- (c) Why has group zero been placed at the extreme right of the periodic table?

OR

What are the disadvantages of the present form of periodic table?

SECTION-E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31. Attempt any five of the following :

- (a) Differentiate between sigma (σ) and pi (π) bond.
- (b) Why is sigma bond stronger than π -bond? Explain.
- (c) Write any two important conditions essential for the linear combination of atomic orbitals.
- (d) Arrange the following bonds in order of increasing ionic character, giving reason.



- (e) Explain why the reactivity of elements of group 1 increases while that of group 17 elements decreases on descending the group.
- (f) An element A belongs to the third period of p-block. It has 3 electrons in the outermost shell. Identify the element and state whether it is a metal or non-metal.
- (g) Write the IUPAC name and symbol for the element with atomic number 120.
- 32. (a)** Elements A, B, C and D have atomic numbers 12, 19, 29 and 36 respectively. On the basis of electronic configuration, which group of the periodic table each element belongs?
- (b)** Predict the blocks to which these elements can be classified. Also predict their periods.

- (c)** Which of these are representative elements?

OR

What were the advantages and limitations of Mendeleev's periodic table? Explain

- 33. On the basis of hybridisation, discuss the structure of the following :**

- (i) PF_5 (ii) C_2H_2 (iii) SF_6
(iv) XeF_4 (v) BrF_5

Also draw the structure.

OR

- (a)** Explain the significance of the bond order. Can bond order be used for quantitative comparisons of the strengths of chemical bonds?

- (b)** Account for the following :

- (i) He_2 is not found to exist in nature.
(ii) N_2^+ is not a diamagnetic substance.
(iii) The dissociation energy of H_2^+ is almost the same as that of He_2^+ .

SOLUTIONS

- 1. (a)** : Anions are larger in size than their parent atom.

- 2. (a)** : Ionic character of compounds of metals increases down the group.

- 3. (c)** : Halogens have highest electron affinity. But electron affinity of Cl is greater than that of F.

- 4. (c)**

- 5. (d)**

- 6. (c)**

- 7. (c)**

- 8. (b)**

- 9. (a)** : NO has 15 electrons out of which one electron remains unpaired.

- 10. (c)**

- 11. (a)** : Metallic character increases down the group and decreases across a period.

- 12. (c)**

- 13. (c)** : Ionisation enthalpy increases along a period, ionisation enthalpy of the extreme left elements in a period is the lowest.

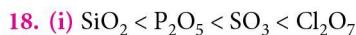
- 14. (a)**

- 15. (b)**

- 16. (c)**

- 17.** Atomic radii decrease across a period. Cations are smaller than their parent atoms. Among isoelectronic species, the one with the larger positive nuclear charge will have a smaller radius.

Hence, the largest species is Mg; the smallest one is Al^{3+} .



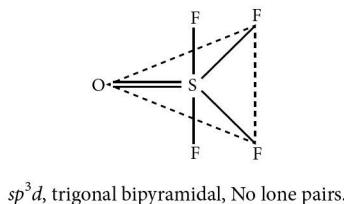
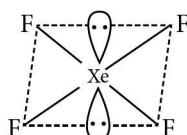
19. In XeF_4 , total number of electron pairs around

$$\text{Xe} = \frac{8+4}{2} = 6$$

Hence, hybridisation of the central atom Xe is sp^3d^2 .

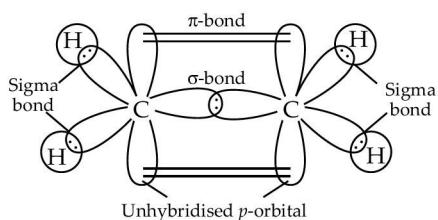
In OSF_4 , the number of electron pairs around the central atom is $6 + 4 / 2 = 5$

Thus, the hybridisation of central atom S is sp^3d .

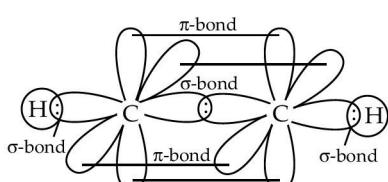


OR

C_2H_4 molecule :



C_2H_2 molecule :



20. Dipole moment, $\mu = q \times d$

$$\therefore 3.336 \times 10^{-29} = q \times 2.6 \times 10^{-10}$$

$$\therefore q = \frac{3.336 \times 10^{-29}}{2.6 \times 10^{-10}} = 1.283 \times 10^{-19} \text{ C}$$

$$\% \text{ ionic character} = \frac{1.283 \times 10^{-19}}{1.602 \times 10^{-19}} \times 100 = 80.09\%$$

21. (i) X : $1s^2 2s^2 2p^6 3s^2 3p^4$, Y : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

(ii) Y belongs to s-block as the last electron enters in 4s orbital.

(iii) X belongs to p-block as the last electron enters in 3p orbital.

22. (a) Electronic configuration of C : $1s^2, 2s^2, 2p^2$
Electronic configuration of B : $1s^2, 2s^2, 2p^1$

The first ionization energy of C will be higher than that of B, because the size of C is smaller than that of B. Thus, the valence electron of C atom feels greater nuclear charge as compared to the valence electron of B. So, it requires higher energy to remove the valence electron of C atom.

Check Your Study Habits to Ace in Physical Chemistry

Study Habits	😊	可以更好
1. Make notes containing key points while attending classes.		
2. Go through the class notes on a regular basis.		
3. Write formulae and conversion factors on daily basis.		
4. Memorise the concepts and theories whenever possible.		
5. Study various concepts in different authentic books and practice them in your own words.		
6. Practice different types of numerical problems based on a particular concept on daily basis.		
7. Make flashcards of important formulae and conversion factors and stick on your notice board.		
8. Avoid rote learning and seek a deeper understanding of a particular concept through books or digital material.		
9. Make a study group where you can actively participate to solve your doubts.		
10. Do not rush too quickly in learning more number of concepts, instead divide a particular chapter into smaller sections and acquire mastery on a particular section.		

Rate Yourself : If your score is

> 9 😊	7-9 😊	5-6 😊	< 5 😊
Excellent	Very good	Good	Needs improvement

After removal of one electron,
 $C^+ : 1s^2 2s^2 2p^1$ and $B^+ : 1s^2 2s^2$

B^+ is extra stable due to fully filled electronic configuration. Thus, removal of electron from B^+ is difficult thus it will have a higher ionization enthalpy than C^+ .

(b) The alkali metals after loss of one electron achieve stable configuration of noble gases. The removal of second electron requires very high energy.

23. (i) The penetration of $2s$ -electron to the nucleus is more than that of a $2p$ -electron. Hence, the $2p$ electron of boron is more shielded from the nucleus by the inner core of electrons than the $2s$ electrons of beryllium. Therefore, it is easier to remove the $2p$ -electron from boron as compared to the removal of a $2s$ -electron from beryllium. Thus, boron has a smaller first ionization enthalpy than beryllium.

(ii) Electron gain enthalpy becomes more negative with increase in the atomic number across a period. The effective nuclear charge increases from, left to right across a period and consequently it will be easier to add an electron to a smaller atom.

24. (a) In the gaseous state, the atoms are widely separated therefore, interatomic forces are minimum. It is because of this reason the term isolated gaseous atom has been included in definition of ionisation enthalpy.

(b) Sodium has eleven electrons and eleven protons but number of protons in Mg^+ are twelve, though it has eleven electrons. Due to higher effective nuclear charge in case of Mg^+ , the removal of electron from it requires more energy.

(c) Elements in the same group in the periodic table have similar physical and chemical properties because their atoms have the same number of electrons in the outermost shell.

OR

(a) Electronegativity increases on moving from left to right in a period. This is due to increase in nuclear charge and decrease in size of atom.

(b) Ionisation enthalpy decreases in a group from top to bottom due to increase in size of atom which results in lesser force of attraction between the nucleus and the outermost shell.

(c) Metallic character decreases and non-metallic character increases from left to right in a period due to increase in ionisation enthalpy and electron gain enthalpy.

25. Applications of dipole moment are :

(i) To decide polarity of the molecule : Molecules having zero dipole moment are said to be non-polar molecules and those having $\mu \neq 0$ are polar in nature.

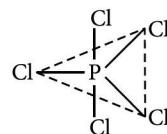
(ii) To determine percentage of ionic character :

Percentage of ionic character

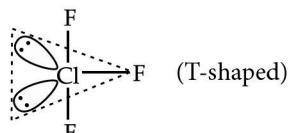
$$= \frac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}} \times 100$$

(iii) To determine geometry of molecules : The values of dipole moments provide valuable information about the structures of molecules. e.g., CO_2 , CS_2 are linear as values of their dipole moments are zero. H_2O is non-linear as it has a net dipole moment.

26. (i) PCl_5 has trigonal bipyramidal structure.



(ii) ClF_3 has trigonal bipyramidal geometry.

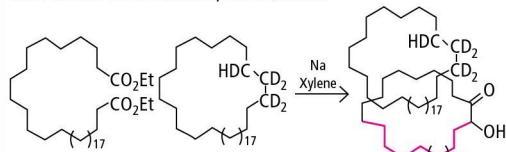


(iii) XeF_4 has octahedral geometry.

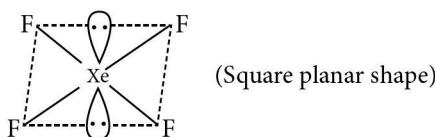
Chemistry bulletin

New results vindicate suspect 63-year-old claim on synthesis of first catenane

Over six decades after Edel Wasserman from Bell Telephone Laboratories claimed to have made the first mechanically interlocked hydrocarbon rings – without direct evidence – UK chemists have supported his findings. For six years David Leigh's team at the University of Manchester sought to show that Wasserman's 1960 letter to the Journal of the American Chemical Society was wrong. In it, the US chemist claimed the first interlocked pair of rings, which he called a catenane. But after Leigh's group painstakingly reproduced Wasserman's work, 'it must have been formed in his reaction', he concludes.



A catenane is a mechanically interlocked molecule consisting of two or more interlocked rings. The word catenane is derived from the Latin word *catena* meaning chain.



27. Salient features of molecular orbital theory (MOT):

- The electrons in molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- An atomic orbital is monocentric while a molecular orbital is polycentric.
- The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two

atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbital while the other is called antibonding molecular orbital.

(v) The bonding molecular orbital has lower energy and hence, greater stability than the corresponding antibonding molecular orbital.

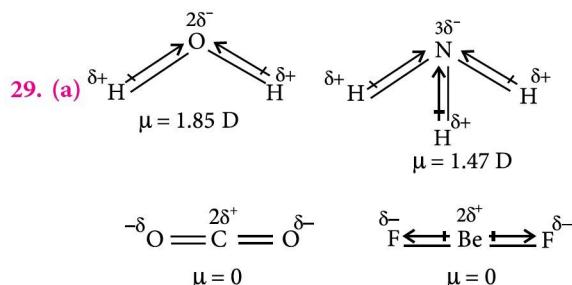
(vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.

(vii) The molecular orbital is like atomic orbitals are filled in accordance with the Aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.

28.

Species	Total electrons	Configuration	Bond order	Magnetic character
O ₂	16	$KK\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^1$	$\frac{(8-4)}{2} = 2.0$	Paramagnetic
O ₂ ⁺	15	$KK\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1$	$\frac{(8-3)}{2} = 2.5$	Paramagnetic
O ₂ ⁻	17	$KK\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^2 = \pi^* 2p_y^1$	$\frac{(8-5)}{2} = 1.5$	Paramagnetic
O ₂ ²⁻	18	$KK\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^2 = \pi^* 2p_y^2$	$\frac{(8-6)}{2} = 1.0$	Diamagnetic

Therefore relative order of stability is O₂⁺ > O₂ > O₂⁻ > O₂²⁻



OR

In AX₃, the dipole moment is zero although the A—X bonds are oriented at an angle of 120° to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third.

(b) CH₃Cl as dipole moment of CCl₄ is zero.

(c) Geometry of CO₂ molecule is linear. So, the resultant dipole moment becomes zero.

But H₂O is a bent structure due to which the dipole moment adds up. Hence H₂O is polar molecule.

30. (a) The particular elements with similar physical and chemical properties are placed in the same group in the periodic table.

(b) In modern periodic table, elements have been placed in order of their increasing atomic numbers. The atomic number of argon is 18 and that of potassium is 19. Thus, argon has been placed before potassium.

(c) The entire periodic table is classified in 18 groups based on their electronic configuration and their reactivity. But zero group elements have stable electronic configuration, they have complete octet and are non-reactive. These are called noble gases or inert elements and do not generally exhibit any chemical reactivity in normal conditions, owing to their electronic configuration, they cannot be classified amongst any of the categories.

OR

Although this periodic table provided a systematic way to study the chemistry of elements and removed most of the anomalies of Mendeleev's and other modern periodic tables, yet it suffers from the following defects:

- In this periodic table, the position of hydrogen is not clear, although it is placed in a separate box just above the group-1.

- Lanthanoids and actinoids have not been merged within the main body of the periodic table.

31. (a) Comparison between σ and π bonds :

	Sigma bond	Pi bond
1.	The bond is formed by the overlap of orbitals along their axes (end to end overlap).	The bond is formed by sidewise overlapping of orbitals (lateral overlapping).
2.	It is a strong bond.	It is a weak bond.

(b) The strength of a bond depends upon the extent of overlapping. Since in the formation of σ -bond, overlapping is along the internuclear axis, therefore there is considerable overlapping. Hence, the σ -bond is a strong bond. On the other hand, in case of the formation of a π -bond, sideways overlapping takes place which is only to a small extent. Hence, π -bond is a weak bond.

(c) (i) The symmetry and relative energies of combining atomic orbitals A and B must be close to each other.

(ii) The extent of overlap between the charge clouds of A and B should be large.

(d) Greater the difference in electronegativity of bonded atoms, more is the ionic character of covalent bond. Hence, the increasing order of ionic character is : C — H < N — H < O — H < F — H

(e) Reactivity of elements of group 1 is high due to their extremely low ionisation enthalpies. The ionisation enthalpies further decrease on descending the group, and hence the reactivity increases down the group.

On the other hand, reactivity of group 17 elements is due to their more negative electron gain enthalpies. Electron gain enthalpies decrease on descending the group and hence the reactivity decreases down the group.

(f) As it has 3 electrons in the outermost shell and it belongs to third period of p -block, hence the outermost shell electronic configuration of A is $3s^23p^1$. Complete electronic configuration is $1s^22s^22p^63s^23p^1$. Hence, atomic number of A is 13, the element is aluminium. It is a metal.

(g) IUPAC name – Unbinilium, Symbol-Ubn

32. (a)

Element	At. No.	Electronic configuration	Group
A	12	$1s^22s^22p^63s^2$	2
B	19	$1s^22s^22p^63s^23p^64s^1$	1
C	29	$1s^22s^22p^63s^23p^63d^{10}4s^1$	11
D	36	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$	18

(b) (i) A receives the last electron in $3s$ -orbital, therefore, it belongs to s-block. Period = 3rd.

(ii) B receives the last electron in $4s$ -orbital, therefore, it belongs to s-block. Period = 4th.

(iii) C receives the last electron in $3d$ -orbitals, therefore, it belongs to d-block. Period = 4th.

(iv) D receives the last electron in the $4p$ -orbital, therefore, it belongs to p-block. Period = 4th.

(c) The elements A, B and D are representative elements.

OR

Advantages of Mendeleev's periodic table are as follows :

Systematic study of elements : This table provides a simple and systematic way to study the elements and their compounds in the form of just 8 groups i.e., by studying the properties of one group or family, the properties of all other elements of the group can be easily predicted.

Correction of atomic weights : This table was also found helpful in correcting the atomic masses of some elements on the basis of their position in the periodic table e.g., atomic mass of beryllium was corrected from 13.5 to 9. Similarly, with the help of this table, atomic masses of indium, gold, platinum, etc. were corrected.

Prediction of new elements : While arranging the elements in the form of periodic table, Mendeleev left some gaps for the undiscovered elements as he focused on his primary aim of arranging the elements having similar properties in the same group. He also predicted the properties of these undiscovered elements on the basis of their position.

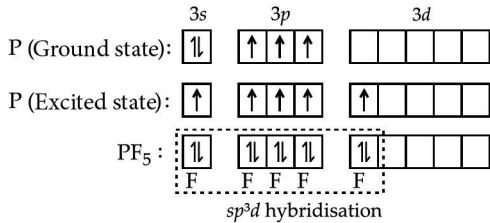
Limitations of Mendeleev's periodic table are as follows :

Position of hydrogen : In Mendeleev's periodic table, hydrogen is placed in group IA, although it shows similarity in properties with the elements of group IA as well as with the elements of group VIIA. Therefore in this periodic table, the position of hydrogen is not clearly defined.

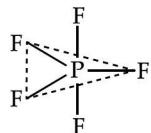
Inversion in the periodic table : In order to satisfy the periodic law, in this table certain pairs of elements

had to be placed in the reverse order of atomic weights e.g., cobalt (atomic weight 58.9) has been placed before nickel (atomic weight 58.7).

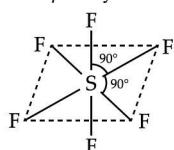
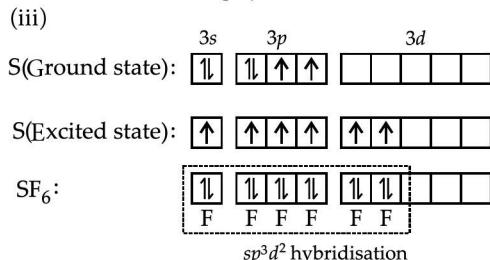
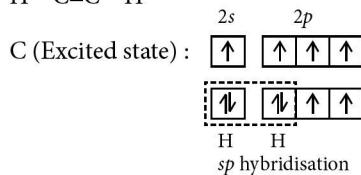
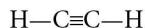
33. (i) Formation of PF_5 (sp^3d hybridisation)



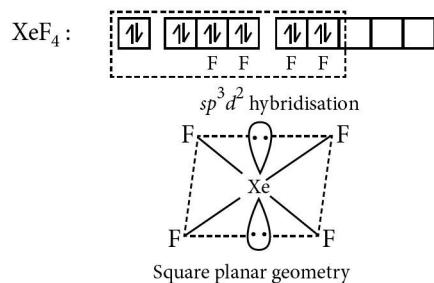
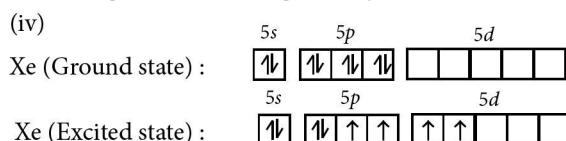
The shape of the molecule is trigonal bipyramidal and all the bond angles are not equal. Three P—F bonds lie in one plane with 120° angle and are called equatorial bonds while two P—F bonds which lie above and below the equatorial bonds are called axial bonds.



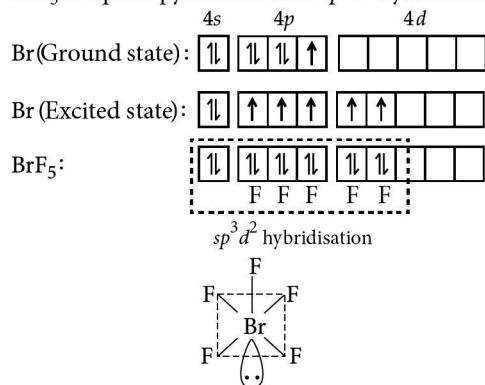
(ii) Each C-atom is sp -hybridised in C_2H_2 . The molecule is linear with a bond angle of 180° .



It has a regular octahedral geometry.



(v) BrF_5 is square pyramidal with sp^3d^2 hybridisation.



OR

(a) Bond order is defined as one-half the difference between the number of electrons present in the bonding and the antibonding molecular orbitals.

$$\text{B.O.} = \frac{N_b - N_a}{2}$$

(i) A positive bond order means a stable molecule while a negative or zero bond order means an unstable molecule.

(ii) Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively. Higher the bond order, greater is bond stability.

(b) (i) In He_2 total 4 electrons are present. Its M.O. electronic configuration is $\sigma 1s^2 \sigma^* 1s^2$. As $N_b = N_a$, the bond order is zero. Hence, He_2 does not exist.

(ii) The M.O. electronic configuration of N_2^+ (total electrons = 13) is

$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^1$$

As one unpaired electron is present in $\sigma 2p_z$ MO, N_2^+ cannot be diamagnetic, it is paramagnetic in nature.

(iii) The bond dissociation energy is directly related to the bond order.

The bond order of H_2^+ is 1/2 and the bond order of He_2^+ ($\sigma 1s^2 \sigma^* 1s^1$) is also 1/2. As bond order is same, the bond dissociation energy of H_2^+ is almost same as that of He_2^+ .





for

NEET/JEE

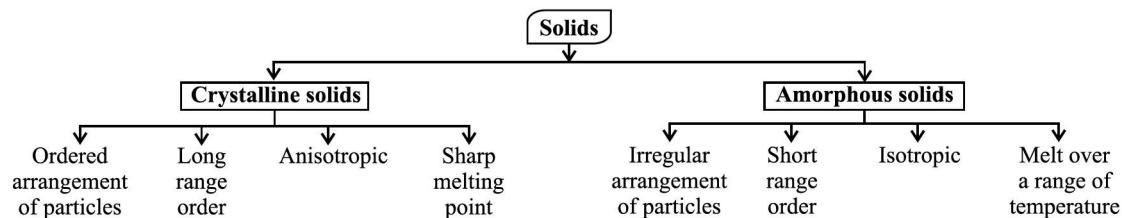
Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 2

The Solid State | Solutions

THE SOLID STATE

- The solid state represents the physical state of matter in which constituents have no translatory motion although vibratory or rotational motions are possible about their positions in solid lattice.
- On the basis of arrangement of constituent particles, solids are classified as :



- When the properties of solid, such as mechanical strength, refractive index and electrical conductivity, etc. are same in all directions, the solid is said to be isotropic. And when these properties are different in different directions, the solid is said to be anisotropic.
- Besides crystalline and amorphous solids, there are some solids which apparently appear amorphous but have microcrystalline structures. These are called polycrystalline solids. Metals often occur in polycrystalline conditions. Individual crystals are randomly oriented so a metallic sample may appear to be isotropic even though a single crystal is anisotropic.

Characteristics of Different Types of Unit Cells (a is the Edge Length of Unit Cell)

Characteristics	Simple Cubic	bcc	fcc
Lattice points (Z)	1	2	4
Coordination number	6	8	12
Packing efficiency	52.4%	68%	74%
Radius (r)	$\frac{a}{2}$	$\frac{\sqrt{3}}{4}a$	$\frac{a}{2\sqrt{2}}$

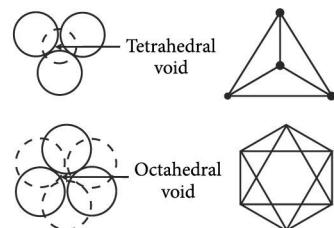
Seven Primitive Unit Cells and their Possible Variations as Centred Unit Cells

Crystal System	Possible Variations	Axial Distances or Edge Lengths	Axial Angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO ₂ , TiO ₂ , CaSO ₄

Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO_3 , BaSO_4
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Graphite, ZnO , CdS ,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO_3), HgS (cinnabar)
Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3

TYPES OF Voids

- Tetrahedral void** is a simple triangular void surrounded by four spheres. In *ccp*, tetrahedral voids are located on body diagonals, two on each body diagonals at one-fourth of the distance from each end.
- Octahedral void** is a double triangular void surrounded by six spheres. In *ccp*, octahedral voids are located at the body centre and edge centres.
- If N is the number of close packed spheres, then the number of octahedral voids generated = N ; the number of tetrahedral voids generated = $2N$
- Radius (r) of tetrahedral void = $0.225 R$;
Radius (r) of octahedral void = $0.414 R$;
where, R is the radius of the spheres in close packing.



- Radius ratio rule :** It refers to the ratio of radius of cation to the radius of anion.

$$\text{Radius ratio} = \frac{\text{Radius of the cation } (r_+)}{\text{Radius of the anion } (r_-)}$$

This rule helps in calculating the coordination number of any compound which further helps in determining the arrangement of ions of different types of crystal structures.

Radius ratio	C. No.	Structural arrangement	Examples
0.155 – 0.225	3	Triangular Planar	Boron trioxide (B_2O_3)
0.225 – 0.414	4	Tetrahedral	Sphalerite (ZnS)
0.414 – 0.732	6	Octahedral	Rock salt (NaCl)
0.732 – 1.000	8	Body centred cubic	Caesium chloride (CsCl)

Packing Fraction

$$f = \frac{\text{Volume of one sphere in the unit cell}}{\text{Volume of the unit cell } (V)} = \frac{Z \times \frac{4}{3}\pi r^3}{a^3}$$

Relation between Density and Edge of Cubic Crystals

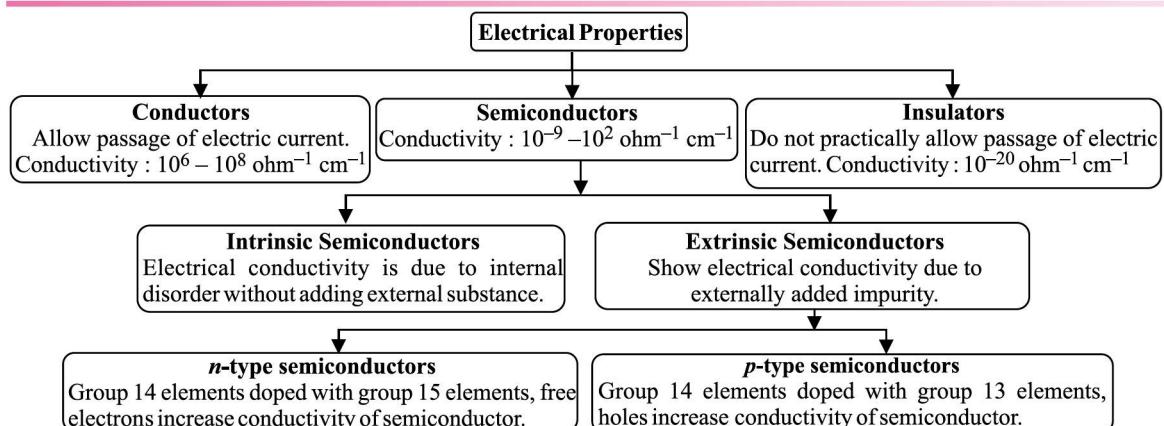
$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

- For elements :** Z = No. of atoms/unit cell (1 for simple, 2 for *bcc* and 4 for *fcc*) where, M = Atomic mass of the element; a = Edge length of the unit cell; N_A = Avogadro's number.
- For ionic compounds :** Z = No. of formula units in one unit cell e.g., 4 for NaCl and ZnS , 1 for CsCl etc.,
 M = Formula mass (molecular mass) of the compound,
 a = Edge length = $2 \times$ distance between Na^+ and Cl^- in case of NaCl .

IMPERFECTION IN CRYSTALS

Defect	Nature of Defect
Schottky	Atom or ion missing from the lattice point and thus giving a vacancy. Density of the crystal is lowered.
Interstitial	Atom or ion present in a vacant void, also called hole (or interstitial site).
Frenkel	This is a hybrid type of defect produced from the combination of vacancy defect and interstitial defect. Atom or ion at the lattice point displaced to an interstitial site creating a vacancy.
<i>F</i> -centre	Electron trapped in an anionic vacancy is called <i>F</i> -centre. If the concentration of <i>F</i> -centres is high, colourless crystals (like KCl, LiCl, NaCl) develop some colour.
Dislocation	Line defects are called dislocations.
Non-stoichiometric	It is in cases where the compounds contain the combining elements in a ratio different from that required by their stoichiometric formulae. VO_x ($x = 0.6$ to 1.3), $\text{Fe}_{0.95}\text{O}$.

ELECTRICAL PROPERTIES



Band Theory

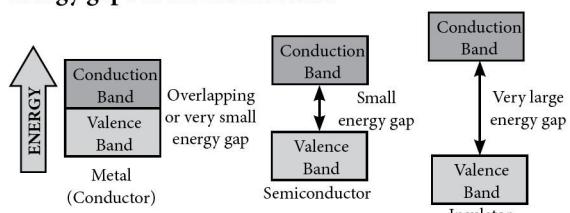
In metals, conductivity strongly depends on the number of valence electrons available per atom. The difference in electrical conductance behaviour of conductors, insulators and semiconductors can be explained with the help of **band theory**.

The atomic orbitals of metal atoms form a large number of molecular orbitals which are so close in energy to each other that they form a band. If the band is partially filled or it overlaps with a higher energy unoccupied band, then electrons can easily flow under an applied electric field and metal shows conductivity.

Therefore, when some electric field is applied, electrons can easily move within partially filled band or empty overlapping band and this movement is responsible for electrical conductance of the substance. This type of behaviour is shown by metals.

In general, the electrical conductance of solids depends

upon the energy gap between the filled valence band and next higher vacant energy band. The outermost filled energy band is called **valence band** and the next empty band in which electrons can move is called **conduction band**. The spaces between valence band and conduction band represent energies forbidden to electrons and are called **energy gaps** or **forbidden zone**.



In **metals**, the conduction band is close to valence band and, therefore, the electrons can easily go into the conduction band. Therefore, metals are good **conductors**.

In **insulators**, the energy gap between valence band and conduction band is very large.

Semiconductors have only small difference in energy between the filled valence band and empty conduction band.

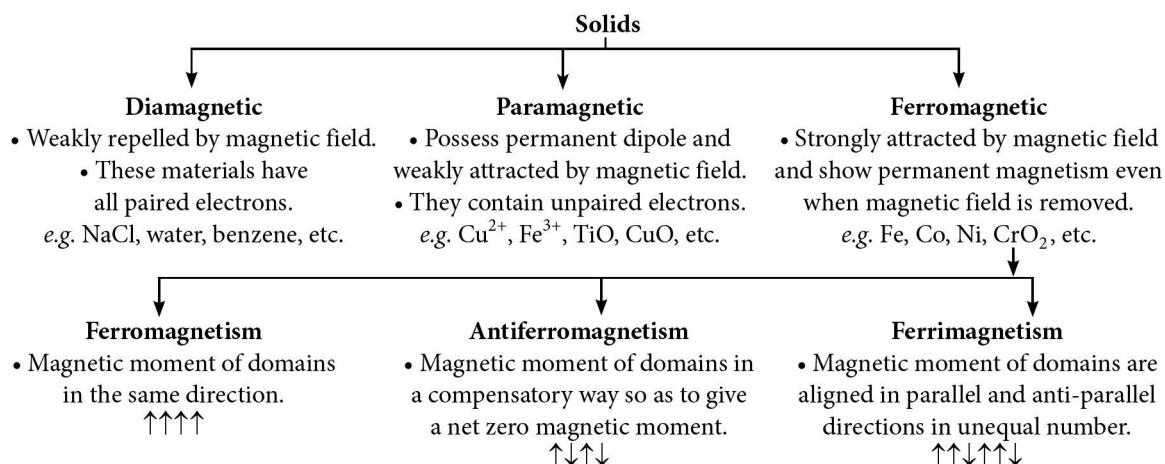
Electrical conductivity of semiconductors increases with rise in temperature because more electrons can jump to the conduction band.

Conductivity of semiconductors can also be increased by **doping** i.e., a process of adding impurities to a crystalline substance to change its properties. Impurities are either electron rich or electron deficient. The semiconductors thus obtained are :

- **n-type semiconductors** : When group-14 elements are doped with group-15 elements (conductivity due to electrons). e.g., Silicon doped with phosphorus.
- **p-type semiconductors** : When group-14 elements are doped with group-13 elements. (conductivity due to holes). e.g., Germanium doped with boron.

MAGNETIC PROPERTIES

Magnetic moment arises due to orbital motion of the electron around the nucleus and spin of electron around its own axis. The magnetic properties of solids are related to the electronic structure. On the basis of response towards magnetic field, solids are divided as follows :



SOLUTIONS

When two or more non-reacting substances are mixed, they form mixtures. A mixture may be heterogeneous or homogeneous. A homogeneous mixture whose composition can be varied within certain limits is termed as **true solution**.

Solution is a mixture of solute and solvent, the component which is present in larger quantity is known as **solvent** and the other one is known as **solute**.

EXPRESSING CONCENTRATION OF SOLUTIONS

The amount of solute present in the given quantity of solution is known as concentration.

- **Molarity** : The molarity of a solution is defined as the number of moles of solute dissolved in one litre of solution. It is denoted by *M*.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$$

$$\text{or Molarity } (M) = \frac{w \times 1000}{M \times V}$$

where, *w* = weight of solute,

M = molecular weight of solute,

V = volume in mL.

Unit of molarity = mol L⁻¹ or mol dm⁻³

- **Molality** : It is defined as moles of solute dissolved per kilogram of the solvent. It is denoted by *m*.

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Weight of solvent in kg}}$$

$$\text{Molality } (m) = \frac{w \times 1000}{M \times W}$$

where, *w* = weight of solute,

M = molecular weight of solute,

W = weight of solvent in g.

- **Mole fraction** : It is the ratio of number of moles of one component to the total number of moles (solute and solvent) present in the solution. It is denoted by *X*.

Thus for a solution containing *n_A* moles of solute and *n_B* moles of solvent, the mole fraction of the

solute (X_A) and solvent (X_B) respectively would be

$$X_A = \frac{n_A}{n_A + n_B}; X_B = \frac{n_B}{n_A + n_B}$$

for a binary solution, $X_A + X_B = 1$

Mole fraction has no unit.

- Solubility** of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature.
- Factors affecting solubility of a solid in a liquid:**
 - Nature of solute and solvent :** Polar solutes dissolve in polar solvents and non-polar solutes in non-polar solvents (*i.e.*, like dissolves like).
 - Effect of temperature :**
 - If the dissolution process is endothermic ($\Delta_{\text{sol}}H > 0$), the solubility increases with rise in temperature.
 - If dissolution process is exothermic ($\Delta_{\text{sol}}H < 0$), the solubility decreases with rise in temperature.
 - The effect of temperature is in accordance with Le Chatelier's principle
 - Effect of pressure :** Pressure does not have any significant effect on solubility of solids in liquids as these are highly incompressible.

- Factors affecting solubility of a gas in a liquid :**

Effect of pressure : Henry's law states that "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution".

$p = K_H x$ where, K_H is the Henry's law constant and is different for different gases at a particular temperature.

Higher the value of K_H at a given pressure, lower is the solubility of the gas in the liquid.

VAPOUR PRESSURE OF SOLUTIONS AND RAOULT'S LAW

- Vapour pressure of liquid-liquid solutions (Raoult's Law) :** It states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

$$P_{\text{total}} = p_1 + p_2 = x_1 p_1^\circ + x_2 p_2^\circ = p_1^\circ + (p_2^\circ - p_1^\circ)x_2$$

p_1 and p_2 are the vapour pressures of component 1 and 2 respectively, whereas p_1° and p_2° are the vapour pressures of pure component 1 and 2 respectively.

- Vapour pressure of solutions of solids in liquids :** Vapour pressure of the solution at a given

temperature is lower than the vapour pressure of the pure solvent at the same temperature.

Ideal and Non-ideal Solutions

Ideal Solutions	Non-ideal Solutions
Obey Raoult's law at all temperatures and concentrations.	Do not obey Raoult's law at all temperatures and concentrations.
$P_1 = x_1 P_1^\circ; P_2 = x_2 P_2^\circ$	$P_1 \neq x_1 P_1^\circ; P_2 \neq x_2 P_2^\circ$
$\Delta H_{\text{mix}} = 0, \Delta V_{\text{mix}} = 0$	$\Delta H_{\text{mix}} \neq 0, \Delta V_{\text{mix}} \neq 0$

Non-ideal Solutions showing Positive and Negative Deviations from Raoult's Law

Solutions showing positive deviation	Solutions showing negative deviation
$A - B \ll A - A$ or $B - B$ interactions	$A - B \gg A - A$ or $B - B$ interactions
$\Delta H_{\text{mix}} > 0, \Delta V_{\text{mix}} > 0$	$\Delta H_{\text{mix}} < 0, \Delta V_{\text{mix}} < 0$
$P_i > P_i^\circ x_i$	$P_i < P_i^\circ x_i$
form minimum boiling azeotropes	form maximum boiling azeotropes

Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called minimum boiling azeotrope and maximum boiling azeotrope. The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition. For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, known as azeotrope composition, has been achieved, the liquid and vapour have the same composition, and no further separation occurs.

The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

COLLIGATIVE PROPERTIES

Properties which depend on the number of solute particles irrespective of their nature relative to the

total number of particles present in the solution. Such properties are called colligative properties. A solution has four colligative properties

- Relative lowering of vapour pressure :

$$\frac{\frac{P_A^{\circ} - P_A}{P_A^{\circ}}}{x_B} = x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A} = \frac{W_B \times M_A}{M_B \times W_A}$$

(∴ for dilute solutions, $n_B << n_A$)

- Elevation in boiling point : $\Delta T_b = T_b - T_b^c$

$$\Delta T_b \propto m \text{ or } \Delta T_b = K_b m = K_b \left(\frac{W_B \times 1000}{M_B \times W_A} \right)$$

or $M_B = \frac{1000 \times W_B \times K_b}{\Delta T_b \times W_A}$

K_b is called boiling point elevation constant or molal elevation constant or Ebulloscopic constant, having unit K kg mol^{-1} .

- Depression in freezing point : $\Delta T_f = T_f^\circ - T_f$

$$\Delta T_f \propto m \text{ or } \Delta T_f = K_f m = K_f \left(\frac{W_B \times 1000}{M_B \times W_A} \right) \text{ or}$$

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

K_f is known as freezing point depression constant or molal depression constant or Cryoscopic constant, having unit K kg mol^{-1} .

- #### **• Osmosis and osmotic pressure :**

$$\pi = CRT = \left(\frac{n_B}{V} \right) RT$$

$$\pi V = \frac{W_B RT}{M_p} \text{ or } M_B = \frac{W_B RT}{\pi V}$$

[NOTE : Suffix A denotes solvent and B denotes solute.]

van't Hoff factor

- It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

$$i = \frac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$$

Total number of moles of particles after

$$i = \frac{\text{association/dissociation}}{\text{Number of moles of particles before}}$$

Number of moles of particles before

association/dissociation

For association, $i < 1$; For dissociation, $i > 1$.

- Relation between van't Hoff factor and degree of dissociation : $\alpha = \frac{i-1}{n-1}$
 - Relation between van't Hoff factor and degree of association : $\alpha = \frac{1-i}{1-1/n}$
 - Modified equations for colligative properties :

$$\frac{p_A^\circ - p_A}{p_A^\circ} = i \cdot \frac{n_B}{n_A},$$

$$\Delta T_b = iK_b m, \Delta T_f = iK_f m, \pi = i n_B RT/V$$



WRAP it up!

MCQs TYPE QUESTIONS

density of A to that of B is 1.6 while the ratio of the edge length of B to that of A is 2. If the molar mass of crystal B is 200 g mol^{-1} , then that of crystal A is

4. Match the column I with column II and mark the appropriate choice.

	Column I	Column II
(A)	$\Delta H_{\text{mix}} = 0, \Delta V_{\text{mix}} = 0$	(i) Non-ideal solution
(B)	$\Delta H_{\text{mix}} \neq 0, \Delta V_{\text{mix}} \neq 0$	(ii) Positive deviation
(C)	$\Delta H_{\text{mix}} < 0, \Delta V_{\text{mix}} < 0$	(iii) Ideal solution
(D)	$\Delta H_{\text{mix}} > 0, \Delta V_{\text{mix}} > 0$	(iv) Negative deviation

- (a) (A) \rightarrow (i), (B) \rightarrow (iii), (C) \rightarrow (ii), (D) \rightarrow (iv)
 (b) (A) \rightarrow (iii), (B) \rightarrow (i), (C) \rightarrow (iv), (D) \rightarrow (ii)
 (c) (A) \rightarrow (ii), (B) \rightarrow (iii), (C) \rightarrow (iv), (D) \rightarrow (i)
 (d) (A) \rightarrow (iii), (B) \rightarrow (ii), (C) \rightarrow (i), (D) \rightarrow (iv)

5. Which of the following statements for crystals having Frenkel defect is not correct?
 (a) Frenkel defects are observed where the difference in sizes of cations and anions is large.
 (b) The density of crystals having Frenkel defect is lesser than that of a pure perfect crystal.
 (c) Ionic substances like ZnS, AgCl and AgBr show Frenkel defect.
 (d) None of these.

6. Which of the following statements is correct?
 For 0.1 M solution of each,
 (a) osmotic pressure of NaCl and Na_2SO_4 solution will be same
 (b) osmotic pressure of NaCl solution will be more than Na_2SO_4 solution
 (c) osmotic pressure of Na_2SO_4 solution will be more than NaCl solution
 (d) osmotic pressure of Na_2SO_4 could be less or more than that of NaCl solution.

7. Which of the following statements is not true about the voids?
 (a) Octahedral void is formed at the centre of six spheres which lie at the apices of a regular octahedron.
 (b) There is one octahedral site for each sphere.
 (c) There are two tetrahedral sites for each sphere.
 (d) Octahedral voids are formed when the triangular voids in second layer exactly overlap with similar voids in the first layer.

8. A solution containing 0.1 g of non-volatile organic substance P (molecular weight 100) in 100 g of benzene raises the boiling point of benzene by 0.2°C while a solution containing 0.1 g of another non-volatile substance Q in the same amount of benzene raises the boiling point of benzene by 0.4°C . What is the ratio of the molecular weights of P and Q?
 (a) 1 : 2 (b) 2 : 1 (c) 1 : 4 (d) 4 : 1

9. The unit cell of aluminium is a cube with an edge length of 405 pm. The density of aluminium is 2.70 g cm^{-3} . What is the structure of unit cell of aluminium?
 (a) Body-centred cubic cell
 (b) Face-centred cubic cell
 (c) End-centred cubic cell
 (d) Simple cubic cell

- 10.** The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be
 $(K_f \text{ for benzene} = 5.12\text{ K kg mol}^{-1})$
(a) 74.6% (b) 94.6% (c) 64.6% (d) 80.4%

11. A metal crystallises with a face-centred cubic lattice. The edge length of the unit cell is 408 pm . The diameter of the metal atom is
(a) 288 pm (b) 408 pm
(c) 144 pm (d) 204 pm

12. **Assertion :** Acetone and aniline show negative deviation.
Reason : H-bonding between acetone and aniline is stronger than that between acetone-acetone and aniline-aniline.
(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

13. Potassium has a *bcc* structure with nearest neighbour distance 4.52 \AA . Its atomic weight is 39 . Its density will be
(a) 454 kg m^{-3} (b) 804 kg m^{-3}
(c) 852 kg m^{-3} (d) 910 kg m^{-3}

14. Arrange the following solutions in the increasing order of their osmotic pressure.
(i) 34.2 g/L sucrose ($M = 342$)
(ii) 60 g/L urea ($M = 60$)
(iii) 90 g/L glucose ($M = 180$)
(iv) 117 g/L NaCl ($M = 58.5$)
(a) Sucrose < Urea < Glucose < NaCl
(b) Sucrose < Glucose < NaCl < Urea
(c) Sucrose < Glucose < Urea < NaCl
(d) NaCl < Urea < Glucose < Sucrose

15. Molecules/ions and their magnetic properties are given below.

Molecule/ion	Magnetic property
(i) C_6H_6	(1) Antiferromagnetic
(ii) CrO_2	(2) Ferrimagnetic
(iii) MnO	(3) Ferromagnetic
(iv) Fe_3O_4	(4) Paramagnetic
(v) Fe^{3+}	(5) Diamagnetic

The correctly matched pairs in the above is
(a) i-5, ii-3, iii-2, iv-1, v-4

- (b) i-3, ii-5, iii-1, iv-4, v-2
 (c) i-5, ii-3, iii-1, iv-2, v-4
 (d) i-5, ii-3, iii-1, iv-4, v-2
- 16.** How many total constituent particles are present in simple cubic unit cell?
 (a) 1 (b) 3 (c) 4 (d) 2
- 17.** Given below are two statements:
Statement-I : Frenkel defects are vacancy as well as interstitial defects.
Statement-II : Frenkel defect leads to colour in ionic solids due to presence of F -centres.
 Choose the most appropriate answer for the statements from the options given below:
 (a) Statement-I is false but statement-II is true.
 (b) Both statement-I and statement-II are false.
 (c) Statement-I is true but statement-II is false.
 (d) Both statement-I and statement-II are true.
- 18.** The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is
 (a) 4.0×10^{-4} (b) 4.0×10^{-5}
 (c) 5.0×10^{-4} (d) 4.0×10^{-6}
- 19.** Fe_3O_4 (magnetite) is an example of
 (a) normal spinel structure
 (b) inverse spinel structure
 (c) fluorite structure
 (d) antifluorite structure.
- 20.** Two liquids X and Y form an ideal solution. The mixture has a vapour pressure of 400 mm at 300 K when mixed in the molar ratio of 1 : 1 and a vapour pressure of 350 mm when mixed in the molar ratio of 1 : 2 at the same temperature. The vapour pressures of the two pure liquids X and Y respectively are
 (a) 250 mm, 550 mm (b) 350 mm, 450 mm
 (c) 550 mm, 250 mm (d) 500 mm, 500 mm
- NUMERICAL VALUE TYPE QUESTIONS**
- 21.** In 100 g of naphthalene, 2.423 g of S was dissolved. Melting point of naphthalene = 80.1 °C. $\Delta T_f = 0.661^\circ\text{C}$, $L_f = 35.7 \text{ cal/g}$ of naphthalene. If the molecular formula of sulphur added is S_x the value of x is _____.
22. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallizes in a body-centered cubic lattice. If the density is 2 g/cc then the radius of metal atom is _____. ($N_A = 6 \times 10^{23}$)
- 23.** x g of a non-electrolytic compound (Molar mass = 200) is dissolved in 1.0 litre of 0.05 M NaCl. The osmotic pressure of this solution is found to be 4.92 atm at 27 °C. The value of x is _____. Assume complete dissociation of NaCl and ideal behaviour of this solution.
 $(R = 0.0821 \text{ litre atm mol}^{-1} \text{ K}^{-1})$
- 24.** A certain element crystallises in a bcc lattice of unit cell edge 27 Å. If the same element under the same conditions crystallises in the fcc lattice, the edge length of the unit cell in Å will be _____. (Round off to the Nearest Integer)
 [Assume each lattice point has a single atom]
 [Assume $\sqrt{3} = 1.73$, $\sqrt{2} = 1.41$]
- 25.** The edge length of the unit cell of NaCl crystal lattice is 5.623 Å and density is 2.16 g cm^{-3} and the molar mass of NaCl is 58.5 g mol $^{-1}$. The number of moles per unit cell is _____.
SOLUTIONS
- 1.** (d): Number of A^+ ions = $\left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) = 4$
 (at corners) (at face centres)
- Number of B^- ions = $(1) + \left(12 \times \frac{1}{4}\right) = 4$
 (at body centre) (at edge centres)
- $$(A^+)_4 (B^-)_4 = A_4B_4 = AB$$
- 2.** (b)
- 3.** (d): Density of the unit cell, $\rho = \frac{Z \times M}{a^3 \times N_0}$
 Given: $\frac{\rho_A}{\rho_B} = 1.6$, $\frac{a_B}{a_A} = 2$, $M_B = 200 \text{ g/mol}$
 $\rho_A = \frac{Z \times M_A}{(a_A)^3 \times N_0}$; $\rho_B = \frac{Z \times M_B}{(a_B)^3 \times N_0}$
 (Z will be same for isomorphous crystals)

$$\frac{\rho_A}{\rho_B} = \frac{M_A}{M_B} \times \left(\frac{a_B}{a_A}\right)^3 \Rightarrow 1.6 = \frac{M_A}{200} \times (2)^3$$

$$M_A = \frac{1.6 \times 200}{8} = 40 \text{ g/mol}$$
- 4.** (b) **5.** (b)
- 6.** (c): $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$, $i = 2$
 $\text{Na}_2\text{SO}_4 \rightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$, $i = 3 \Rightarrow \pi = iCRT$
 For the same concentration, $\pi \propto i$
 Thus, osmotic pressure is more for Na_2SO_4 .
- 7.** (d)

8. (b) : $M = \frac{1000 K_b w_2}{w_1 \times \Delta T_b}$

$$\therefore \frac{M_P}{M_Q} = \frac{(w_2)_P}{(w_2)_Q} \times \frac{(\Delta T_b)_Q}{(\Delta T_b)_P} = \frac{0.1}{0.2} \times \frac{0.4}{0.1} = \frac{2}{1} = 2:1$$

9. (b)

10. (b) : $\Delta T_f = 0.45^\circ\text{C}$

w_2 (acetic acid) = 0.2 g; w_1 (benzene) = 20 g

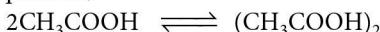
$K_f = 5.12 \text{ K kg mol}^{-1}$

$$\Delta T_f = i \times K_f \times m$$

$$\therefore i = \frac{\Delta T_f}{K_f \times m} = \frac{0.45 \times 20 \times 60}{5.12 \times 0.2 \times 1000}$$

$$i = 0.527$$

According to question,



Initially : 1 mol 0

After time t : $(1 - \alpha)$ mol $\frac{\alpha}{2}$

$$\Rightarrow i = 1 - \alpha + \frac{\alpha}{2}$$

$$i = 1 - \frac{\alpha}{2} \quad \dots(i)$$

On putting the value of i in equation (i), we get

$$0.527 = 1 - \frac{\alpha}{2} \Rightarrow -0.946 = -\alpha; \alpha = 0.946$$

$$\therefore \text{Percentage association of acetic acid in benzene} = 94.6\%$$

11. (a)

12. (a)

13. (d)

14. (c)

15. (c)

16. (a) : A simple cubic lattice has eight atoms on the corners. So, the contribution by each atom = 1/8
Therefore, number of atoms present in the unit cell = $1/8 \times 8 = 1$

17. (c)

18. (a) : According to Henry's law

$x_{\text{N}_2} \times K_{\text{H}} = p_{\text{N}_2}$ (p_{N_2} = Partial pressure of N_2)

Given, total pressure = 5 atm

Mole fraction of N_2 in air = 0.8

\therefore Partial pressure of $\text{N}_2 = 0.8 \times 5 = 4$

$$\Rightarrow x_{\text{N}_2} \times 1 \times 10^5 = 4 \Rightarrow x_{\text{N}_2} = 4 \times 10^{-5}$$

No. of moles of H_2O , $n_{\text{H}_2\text{O}} = 10$

No. of moles of N_2 , $n_{\text{N}_2} = ?$

$$\frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{H}_2\text{O}}} = x_{\text{N}_2} = 4 \times 10^{-5} \Rightarrow \frac{n_{\text{N}_2}}{10 + n_{\text{N}_2}} = 4 \times 10^{-5}$$

[As $n_{\text{N}_2} \ll 10$]

$$\Rightarrow n_{\text{N}_2} = 4 \times 10^{-4}$$

19. (b)

20. (c)

21. (8) : $M_2 = \frac{1000 K_f w_2}{w_1 \Delta T_f} = \frac{1000 w_2}{w_1 \Delta T_f} \times \frac{RT_f^2}{1000 L_f}$

$w_2 = 2.423 \text{ g}; w_1 = 100 \text{ g}; R = 2 \text{ cal degree}^{-1} \text{ mol}^{-1}$

$T_f = 80.1 + 273 = 353.1 \text{ K}, \Delta T_f = 0.661^\circ\text{C}$,

$L_f = 35.7 \text{ cal/g}$

$$M_2 = \frac{1000 \times 2.423}{100 \times 0.661} \times \frac{2 \times (353.1)^2}{1000 \times 35.7} = 256$$

(Value of R in terms of calories is taken as 2)

As, S_x is given to be the molecular formula of added sulphur

$$\Rightarrow x = \frac{256}{32} = 8$$

Thus, molecular formula of sulphur is S_8 .

22. (217) : $\rho = \frac{ZM}{N_A V}, Z = \frac{\rho N_A V}{M}$

$$Z = \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8})^3}{75} = 2$$

It means, this lattice is bcc.

$$\text{Thus, } r = \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 5 = 2.165 \text{ \AA}$$

$$r = 216.5 \text{ pm} \approx 217 \text{ pm}$$

23. (20) : $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$

Concentration of NaCl solution containing ions

$$= 0.05 \times 2 = 0.1 \text{ M}$$

$$\text{Effective molarity of solution} = \frac{x}{200}$$

$$\pi = CRT$$

$$4.92 = \left(\frac{x}{200} + 0.1 \right) \times 0.0821 \times (27 + 273)$$

$$\Rightarrow x = 19.95 \approx 20 \text{ g}$$

24. (33) : For bcc unit cell, $\sqrt{3}a = 4r$

$$a = \frac{4r}{\sqrt{3}} = 27; r = \frac{27\sqrt{3}}{4}$$

For fcc unit cell, $\sqrt{2}a = 4r$

$$a = \frac{4r}{\sqrt{2}} = \frac{4 \times 27\sqrt{3}}{\sqrt{2} \times 4}; r = 27 \frac{\sqrt{3}}{\sqrt{2}} = 33.1 \approx 33$$

25. (4) : $\rho = \frac{Z \times M}{N_A \times a^3}, Z = \frac{\rho \times N_A \times a^3}{M}$

$$Z = \frac{2.16 \times 6.023 \times 10^{23} \times (5.623 \times 10^{-8})^3}{58.5} = 3.95 \approx 4$$





CBSE warm-up!

CLASS-XII

Chapterwise practice questions for CBSE Exams as per the latest pattern
and rationalised syllabus by CBSE for the academic session 2023-24.

Series-3

Chemical Kinetics

Time Allowed : 3 hours
Maximum Marks : 70

General Instructions

Read the following instructions carefully.

- (a) There are 33 questions in this question paper with internal choice.
- (b) SECTION-A consists of 16 multiple-choice questions carrying 1 mark each.
- (c) SECTION-B consists of 5 short answer questions carrying 2 marks each.
- (d) SECTION-C consists of 7 short answer questions carrying 3 marks each.
- (e) SECTION-D consists of 2 case-based questions carrying 4 marks each.
- (f) SECTION-E consists of 3 long answer questions carrying 5 marks each.
- (g) All questions are compulsory.
- (h) Use of log tables and calculators is not allowed.

SECTION-A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. If initial concentration is reduced to $1/4^{\text{th}}$ in a zero-order reaction, the time taken for half the reaction to complete
 - (a) remains same
 - (b) becomes 4 times
 - (c) becomes one-fourth
 - (d) doubles.
2. Which factor has no influence on the rate of reaction?
 - (a) Molecularity
 - (b) Temperature
 - (c) Concentration of reactant
 - (d) Nature of reactant
3. For a reaction, $pA + qB \rightarrow$ products, the rate law expression is $r = k [A]^m[B]^n$, then
 - (a) $(p+q) \neq (m+n)$
 - (b) $(p+q) = (m+n)$
 - (c) $(p+q)$ may or may not be equal to $(m+n)$
 - (d) $(p+q) > (m+n)$
4. In the reaction,
 $\text{BrO}_3^{-\text{(aq)}} + 5\text{Br}^{-\text{(aq)}} + 6\text{H}^{+\text{(aq)}} \rightarrow 3\text{Br}_2\text{(l)} + 3\text{H}_2\text{O(l)}$
The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as
 - (a) $\frac{d[\text{Br}_2]}{dt} = -\frac{5}{3} \frac{d[\text{Br}^-]}{dt}$
 - (b) $\frac{d[\text{Br}_2]}{dt} = \frac{5}{3} \frac{d[\text{Br}^-]}{dt}$
 - (c) $\frac{d[\text{Br}_2]}{dt} = \frac{3}{5} \frac{d[\text{Br}^-]}{dt}$
 - (d) $\frac{d[\text{Br}_2]}{dt} = -\frac{3}{5} \frac{d[\text{Br}^-]}{dt}$
5. For a first-order reaction, the unit of the rate constant is
 - (a) $\text{mol}^1 \text{L}^{-1} \text{s}^{-1}$
 - (b) $\text{mol}^{-1} \text{L}^1 \text{s}^{-1}$
 - (c) $\text{mol}^{-2} \text{L}^{-1} \text{s}$
 - (d) s^{-1}
6. Which one of the following statements is incorrect about the molecularity of a reaction?

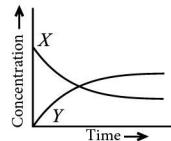
- (a) Molecularity of an elementary reaction is the number of molecules of the reactants present in the balanced equation.
 (b) Molecularity of a reaction is the number of molecules in the slowest step.
 (c) Molecularity is always a whole number.
 (d) There is no difference between order and molecularity of a reaction.
7. The order of reaction is decided by
 (a) temperature
 (b) mechanism of reaction as well as relative concentration of reactants
 (c) molecularity
 (d) pressure.
8. For the reaction $A + B \rightarrow C$, the following data for rate was obtained:

[A]	[B]	Rate (mole/litre sec)
2.0	3.0	0.1
6.0	3.0	0.9
6.0	6.0	0.9

The rate expression from the data is

- (a) $\text{rate} = k [A] [B]^2$ (b) $\text{rate} = k [A]^2$
 (c) $\text{rate} = k [A] [B]$ (d) $\text{rate} = k [B]^2 [A]^0$

9. Figure depicts the change in concentration of species X and Y as a function of time. The point of intersection of the two curves represents
 (a) $t_{1/2}$
 (b) $t_{3/4}$
 (c) $t_{2/3}$
 (d) data insufficient to predict.
10. The activation energy of a reaction is zero. The rate constant of the reaction
 (a) increases with increase of temperature
 (b) decreases with increase of temperature
 (c) decreases with decrease of temperature
 (d) is nearly independent of temperature.



11. For effective collisions, colliding molecules must have
 (a) minimum potential energy
 (b) sufficient kinetic energy
 (c) sufficient potential energy
 (d) maximum energy of activation.
12. The rate constant of a first order reaction is given by
 (a) $k = 2.303 \times t \times \log_{10} \frac{a}{(a-x)}$
 (b) $\frac{k}{t} = 2.303 \log_{10} \frac{a}{(a-x)}$

$$(c) k = \frac{2.303}{t} \log_{10} \frac{1}{(a-x)}$$

$$(d) k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

13. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A): The molecularity of the reaction $H_2 + Br_2 \rightarrow 2HBr$ is 2.
Reason (R): The order of this reaction is 3/2.
 Select the most appropriate answer from the options given below:
 (a) Both A and R are true and R is the correct explanation of A.
 (b) Both A and R are true 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.

14. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A): Order of a reaction with respect to any reactant can be zero, positive, negative or fractional.
Reason (R): Rate of a reaction cannot decrease with increase in concentration of a reactant or a product.
 Select the most appropriate answer from the options given below:
 (a) Both A and R are true and R is the correct explanation of A.
 (b) Both A and R are true 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.

15. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A): Hydrogenation of ethene is an example of zero order reaction.
Reason (R): The rate of zero order reactions is independent of the concentrations of reactants.
 Select the most appropriate answer from the options given below:
 (a) Both A and R are true and R is the correct explanation of A.
 (b) Both A and R are true 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.

16. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A): Hydrolysis of ethyl acetate in presence of acid is a reaction of first order whereas

in presence of alkali, it is a reaction of second order.
Reason (R): Acid only acts as a catalyst whereas alkali acts as one of the reactants.

Select the most appropriate answer from the options given below :

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true 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.

SECTION-B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. What is activation energy? How is it calculated?
18. In a chemical reaction $2P \rightarrow 4Q + R$, the concentration of Q is found to be increased by $2.0 \times 10^{-2} \text{ mol L}^{-1}$ in five seconds. Calculate :
 - (i) rate of appearance of Q
 - (ii) rate of reaction.
19. Differentiate between the rate of a chemical reaction and the rate constant for the reaction.
20. Rate of a reaction $A + B \rightarrow \text{Products}$, increases two fold when concentration of A is doubled and by four fold when concentration of B is doubled. Predict the order of reaction.

OR

How does a change in temperature affect the rate of a reaction? How can this effect on the rate constant of reaction be represented quantitatively?

21. Write the expression for relation between $\log_{10}[R]$ and t for a first order reaction and draw a graph.

SECTION-C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. (i) (a) What is the drawback of collision theory?
(b) Mention the necessary conditions for collision of reactant molecules to give product.
(ii) What is catalyst? What is the effect of catalyst on the rate of a reaction?
23. Show that for a first order reaction, the half-life period is independent of initial concentration.
24. The rate constant for the first order decomposition of H_2O_2 is given by the following equation :

$$\log k = 14.2 - \frac{1.0 \times 10^4 \text{ K}}{T}$$

Calculate E_a for this reaction and rate constant k if its half-life period is 200 minutes.

(Given : $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

25. The decomposition of phosphine has the rate law :
 $4\text{PH}_{3(g)} \longrightarrow \text{P}_{4(g)} + 6\text{H}_{2(g)}$
Rate = $k[\text{PH}_3]$
The rate constant is $6 \times 10^{-4} \text{ s}^{-1}$ at 27°C and activation energy is $3.05 \times 10^5 \text{ J mol}^{-1}$. What is the value of rate constant at 37°C ?
26. An endothermic reaction $A \rightarrow B$ has an activation energy as $x \text{ kJ mol}^{-1}$ of A. If energy change of the reaction is $y \text{ kJ}$, what will be the activation energy of the reverse reaction? Draw the energy diagram.
27. A first order reaction takes 80 minutes for 50% completion. What fraction of a given sample will remain after 2 hours?
28. A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of the reaction.

OR

A certain reaction takes 5 minutes for initial concentration 0.5 mol L^{-1} to become 0.25 mol L^{-1} and another 5 minutes to become 0.125 mol L^{-1} . What is the order and specific rate constant of the reaction?

SECTION-D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. A balanced chemical equation never gives us a true picture of how a reaction takes place as rarely a reaction gets completed in one step. The reactions taking place in one step are called elementary reactions. When a sequence of elementary reactions (called mechanisms) gives us the products, the reactions are called complex reactions.

In elementary reactions (single step process), the order of reaction is equal to stoichiometric coefficients of reactants and products.

In complex reactions (multisteps process), the rate of overall reaction is equal to the rate of slowest step known as rate determining step.

Units of rate constant :

$$k = \frac{\text{Rate}}{[A]^x [B]^y} = \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n};$$

(where $[A] = [B]$)

Answer the following questions :

(a) Define an elementary reaction.

OR

Define complex reactions.

(b) Give an example of elementary reaction.

(c) Find out the unit of rate constant of n^{th} order reaction.

30. The rate of a reaction can be measured experimentally by plotting a graph between the concentration of any of the reactants (or products) as a function of time. Generally, any property which is related to the concentration of one of the species taking part in the reaction is selected and then change in this property is measured as a function of time. The reaction can be easily studied by measuring the concentration at different intervals of time. The concentration at different time intervals can be calculated by first measuring the increase in pressure of the reaction mixture at different intervals of time. The average rate of reaction is determined by change in the concentration of reactants at two different times.

$$\text{Average rate of reaction} = -\frac{\Delta[x]}{\Delta t} = -\frac{x_2 - x_1}{t_2 - t_1}$$

The instantaneous rate of reaction is determined graphically by drawing a tangent to the curve at a point corresponding to the given time. Then the slope of this tangent gives the instantaneous rate of the reaction at that time.

Answer the following questions :

(a) Define average rate of a reaction.

(b) Concentration of a reactant A , changed from 0.44 M to 0.32 M in 25 minutes . What will be the average rate of the reaction during this interval?

(c) For the reaction : $2\text{H}_2\text{O}_{2(aq)} \longrightarrow 2\text{H}_2\text{O}_{(l)} + \text{O}_{2(g)}$ if the initial concentration of H_2O_2 is 0.5 M and its concentration after 5 min is 0.3 M . Then, what will be the rate of decomposition of H_2O_2 ?

OR

For a reaction $2A \rightarrow 3B$, if the rate of formation of B is $x \text{ mole/L}$, then what will be the rate of consumption of A ?

SECTION-E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31. Attempt any five of the following :

(a) Ammonia and oxygen react at high temperature as : $4\text{NH}_{3(g)} + 5\text{O}_{2(g)} \rightarrow 4\text{NO}_{(g)} + 6\text{H}_2\text{O}_{(g)}$
In an experiment, rate of disappearance of

NH_3 is $3.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$. Calculate rate of formation of water.

- (b) Why do pieces of wood burn faster than a log of wood of the same mass?
(c) Which step of a complex reaction is termed as the rate determining step?
(d) What is the basic difference between a reaction intermediate and a transition state?
(e) Define molecularity of a reaction.
(f) Can order of a reaction be fractional?
(g) Find the molecularity of the reaction $\text{Cl} \rightarrow \frac{1}{2} \text{Cl}_2$?

32. (i) State the role of activated complex in a reaction and state its relation with activation energy.
(ii) At room temperature (20°C), milk turns sour in about 64 hours . In a refrigerator at 3°C milk can be stored three times as long before it sours. Estimate the activation energy of the reaction that causes the souring of milk.

OR

(i) The rate constant for a reaction of zero order in A is $0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M ?

(ii) The decomposition of a compound is found to follow a first order rate law. If it takes 15 minutes for 20 percent of original material to react, calculate (a) the specific rate constant, (b) the time at which 10 percent of the original material remains unreacted and (c) the time it takes for the next 20 percent of the reactant left after the first 15 minutes , to react.

33. (i) What is zero order reaction? Give one example of zero order reaction.
(ii) The rate of decomposition of ammonia is found to depend upon the concentration of NH_3 according to the equation

$$-\frac{d[\text{NH}_3]}{dt} = \frac{k_1[\text{NH}_3]}{1 + k_2[\text{NH}_3]}$$

What will be the order of reaction when
(a) concentration of NH_3 is very high?
(b) concentration of NH_3 is very low?

OR

- (i) With the help of an example, explain what is meant by pseudo first order reaction?
(ii) Write expression for rate constant of a zero order reaction and explain the terms involved. What is the unit of rate constant of a zero order reaction?

SOLUTIONS

1. (c) : For zero order reactions, $t_{1/2} = \frac{a}{2k}$ i.e. $t_{1/2} \propto a$.

Therefore, when A is reduced to $\frac{1}{4}$ th, $t_{1/2}$ will become $\frac{1}{4}$ th.

2. (a)

3. (c) : Order of reaction i.e., $(m+n)$ may or may not be equal to molecularity $(p+q)$.

4. (d)

5. (d) : For n^{th} order reaction,

$$\text{Rate} = k[a]^n$$

$$k = \frac{\text{Rate}}{[a]^n} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^n} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{\text{mol}^n \text{L}^{-n}} = \text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$$

When $n = 1$, unit of $k = \text{s}^{-1}$.

6. (d) : Order may or may not be equal to molecularity.

7. (b) : Mechanism of reaction as well as relative concentration of reactants decide that how many concentration terms affect the order of reaction.

8. (b)

9. (a)

10. (d) : If $E_a = 0$, $k = Ae^{-E_a/RT} = Ae^0 = A$,

hence, k becomes independent of T .

11. (b)

12. (d)

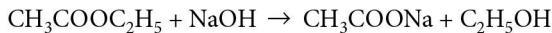
13. (b)

14. (c) : Rate of a reaction increases with increase in concentration of reactants and it also depends on the order of reaction.

15. (d) : Hydrogenation of ethene is an example of first order reaction as, rate = $k[\text{C}_2\text{H}_4]$.

16. (a) : $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$

Rate $\propto [\text{CH}_3\text{COOC}_2\text{H}_5]$



Rate $\propto [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{NaOH}]$

17. The minimum energy required for a reactant molecule to form activated complex is called activation energy. Activation energy is calculated by determining rate of a reaction at two different temperatures using Arrhenius equation.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

18. (i) Rate of appearance of Q

$$\frac{d[Q]}{dt} = \frac{2 \times 10^{-2}}{5} = 0.4 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

Paper Bag Day

12th July

Pollution is defined as the presence of harmful contaminants in the natural environment that causes damage to the living organisms and thereby leads to adverse changes. There is no one, in particular, that we can blame for the increase in pollution except mankind. We, humans, are responsible for the augmented increase of pollution in the environment. Throughout centuries as our civilisation and industrialisation has progressed and found new ways to develop, mother nature has been exploited in a bigger way.

The harmful effluents and substances that are released into the atmosphere by the industries, factories, and household wastes have made an impact in contaminating and deteriorating the environment. One of the major causes of the pollution is the increasing use of plastic bags. Plastic bags are usually difficult as well as costly to recycle and mostly end up on the landfill sites where they take many years to photodegrade. These plastic bags have a tendency to break down into minute toxic particles that contaminate the soil and waterways. By doing so, they enter the food chain when animals accidentally ingest them.

Now-a-days, these plastic bags have been replaced by paper bags. Paper bags have many advantages over plastic bags when it comes to sustainability. Paper bags are comparatively easier to recycle, and not harmful to the environment because they are biodegradable. It is also easier to reuse paper bags and they have a relatively lesser environmental impact. In addition, paper bags are safer, durable, fashionable and are useful in brand promotion and marketing. Also, paper bags are made of renewable raw materials, that encourage a sustainable lifestyle, as they can be recycled. This gives our environment a bit of a break as well.

Paper Bag Day (or World Paper Bag Day) is celebrated on July 12 every year to spread awareness about plastic pollution and encourage the use of environment-friendly alternatives like the paper bag which can be recycled easily and help reduce plastic waste.

HOW CAN WE CELEBRATE PAPER BAG DAY?

1. **Switching to paper bags** : Today, millions of people have already chosen to switch to paper bags for carrying their stuff and other purposes because the widespread use of plastic and its harmful effects on the environment has raised alarm in the society. A lot of brands switched to paper bags to encourage minimal and sustainable packaging, adding an aesthetic quotient to shopping in the process.

2. **Have fun activities with paper bags** : A number of interesting and fun activities can be done by making use of old paper bags. For example, fill a paper bag with different kind of waste materials like leaves, sticks, small rocks, dirt, etc. and carry them from a starting point to the finish line.

3. **Reuse paper bags at home** : Learn how paper bags can be reused in different ways at home. If they are still in good condition, store them carefully so that they can be reused later like covering your books and notebooks.

The following are the major and common uses of paper bags :

- Gift wrapping
- Shopping
- Storing food or other items
- Composting
- Crafting

(ii) Rate of reaction

$$\frac{1}{4} \frac{d[Q]}{dt} = \frac{1}{4} \times 0.4 \times 10^{-2} = 0.1 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

19.

Rate of a reaction	Rate constant
<ul style="list-style-type: none"> It is the speed at which the reactants are converted into products. It is measured as the rate of decrease of concentration of reactant or rate of increase in concentration of the products. 	It is the proportionality constant in the rate law and is defined as the rate of the reaction when the concentration of each of the reactant is unity.
<ul style="list-style-type: none"> It depends upon the initial concentration of the reactant. 	It is independent of the initial concentration of reactant.

20. Rate of reaction increases by two fold when $[A]$ is doubled. Hence, order of reaction w.r.t. A is one. Rate of reaction increases by four fold when $[B]$ is doubled. Hence, order of reaction w.r.t. B is two.

$$\therefore \text{Rate} = k[A][B]^2 \text{ or, order of reaction} = 1 + 2 = 3$$

OR

The rate of reaction is nearly doubled with a rise in temperature by 10° for a chemical reaction. The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation :

$$k = Ae^{-E_a/RT}$$

where $k \rightarrow$ Rate constant

$A \rightarrow$ Arrhenius factor or the frequency factor

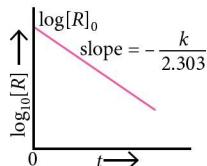
$R \rightarrow$ Gas constant

$T \rightarrow$ Temperature

$E_a \rightarrow$ Energy of activation for the reaction.

21. For first order reaction :

$$\log_{10}[R] = -\frac{k}{2.303}t + \log_{10}[R]_0$$



22. (i) (a) It considers atoms/molecules to be hard spheres and ignores their structural aspects.

(b) The molecules must collide with sufficient kinetic energy and in proper orientation.

(ii) A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent

chemical change. It increases the rate of reaction by decreasing the activation energy.

23. For first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}, \text{ At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$\therefore k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]_0/2} \text{ or, } t_{1/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} \Rightarrow t_{1/2} = \frac{0.693}{k}$$

Thus, in first order reactions, $t_{1/2}$ is independent of initial concentration.

$$\text{24. For first order reaction, } t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = 200 \text{ min} = 200 \times 60 = 12000 \text{ s}$$

$$\Rightarrow k = \frac{0.693}{12000 \text{ s}} = 5.8 \times 10^{-5} \text{ s}^{-1}$$

Also, for first order decomposition of H_2O_2 , rate constant is

$$\log k = 14.2 - \frac{1.0 \times 10^4 \text{ K}}{T}$$

Comparing the above equation with the Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\Rightarrow E_a = 2.303 \times 8.314 \times 1.0 \times 10^4 = 1.91 \times 10^5 \text{ J mol}^{-1}$$

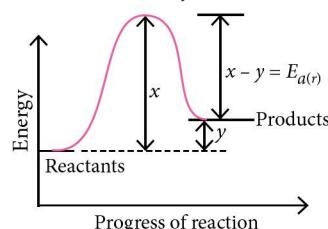
$$\text{25. } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{k_2}{6 \times 10^{-4}} = \frac{3.05 \times 10^5}{2.303 \times 8.314} \left[\frac{10}{300 \times 310} \right] = 1.71282$$

$$\frac{k_2}{6 \times 10^{-4}} = \text{antilog}(1.71282) = 51.62$$

$$k_2 = 6 \times 10^{-4} \times 51.62 = 0.03097 \text{ s}^{-1}$$

26. For an endothermic reaction, activation energy of reversible reaction = $x - y$



$$\text{27. } t_{1/2} = \frac{0.693}{k}$$

$$\Rightarrow k = \frac{0.693}{t_{1/2}} = \frac{0.693}{80 \text{ min}} = 8.6625 \times 10^{-3} \text{ min}^{-1}$$

$$[A]_0 = 1, [A]_t = ?, t = 2 \text{ hours} = 120 \text{ min}$$

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} \Rightarrow 8.6625 \times 10^{-3} = \frac{2.303}{120} \log \frac{1}{[A]_t}$$

$$\log \frac{1}{[A]_t} = 0.4513 \quad \text{or} \quad \frac{1}{[A]_t} = \text{anti log}(0.4513) = 2.827$$

$$[A]_t = 0.35$$

$$\therefore \frac{35}{100} = \frac{7}{20} \text{ fraction will remain after 2 hours.}$$

28. Let initial concentration of the reactant = 100

Thus at $t = 10 \text{ min}$, $a - x = 80$

$t = ?$, when $a - x = 25$

For a first order reaction,

$$k = \frac{2.303}{10} \log \frac{100}{80} = \frac{2.303}{10} \log \frac{5}{4} \quad \dots(i)$$

$$\text{and } k = \frac{2.303}{t} \log \frac{100}{25} = \frac{2.303}{t} \log 4 \quad \dots(ii)$$

From eqn. (i) and (ii),

$$\frac{2.303}{10} \log \frac{5}{4} = \frac{2.303}{t} \log 4$$

$$\text{or } 0.0223 \text{ min}^{-1} = \frac{1.3865}{t}, t = \frac{1.3865}{0.0223} = 62.2 \text{ min}$$

OR

The given data is

$$0.5 \text{ mol L}^{-1} \xrightarrow{5 \text{ min}} 0.25 \text{ mol L}^{-1}$$

$$\xrightarrow{5 \text{ min}} 0.125 \text{ mol L}^{-1}$$

(i) Half life period is independent of initial concentration of the reactant, hence reaction is of first order.

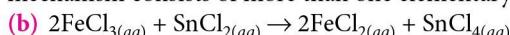
(ii) For first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5 \text{ min}} = 0.138 \text{ min}^{-1}$$

29. (a) The reaction which takes place in a single step is called elementary reaction.

OR

A complex reaction is defined as a reaction whose mechanism consists of more than one elementary step.



(c) Rate (r) = $k[R]^n$; $k = \frac{r}{[R]^n}$

$$\text{Unit of } k = \frac{\text{Unit of } r}{\text{Unit of } [R]^n} = \frac{\text{conc./time}}{[\text{conc.}]^n}$$

$$= [\text{conc.}]^{(1-n)} \text{ time}^{-1} = (\text{mol L}^{-1})^{1-n} \text{ s}^{-1} = \text{mol}^{1-n} \text{ L}^{n-1} \text{ s}^{-1}$$

30. (a) Change in concentration of any substance of a reaction in a certain interval of time is the average rate of a reaction.

(b) Rate = $-\frac{\Delta[A]}{\Delta t} = -\frac{(0.32 - 0.44)}{25} = 4.8 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$

(c) $-\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = -\frac{\text{Final } [\text{H}_2\text{O}_2] - \text{Initial } [\text{H}_2\text{O}_2]}{\text{Elapsed time}}$
 $= \frac{-(0.3 \text{ M} - 0.5 \text{ M})}{5 \text{ min}} = 0.04 \text{ M min}^{-1}$

OR

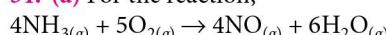
For the reaction, $2A \longrightarrow 3B$

$$\text{Rate of reaction} = -\frac{1}{2} \frac{d[A]}{dt} = \frac{1}{3} \frac{d[B]}{dt}$$

$$\Rightarrow \text{Rate of consumption of } A \left(-\frac{d[A]}{dt} \right)$$

$$= \frac{2}{3} \times \text{rate of formation of } B \left(\frac{d[B]}{dt} \right) = \frac{2x}{3}$$

31. (a) For the reaction,



$$\text{Rate} = -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = -\frac{6}{4} \frac{d[\text{NH}_3]}{dt} = \frac{6}{4} \times \left(-\frac{d[\text{NH}_3]}{dt} \right)$$

$$= \frac{6}{4} \times 3.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} = 5.4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

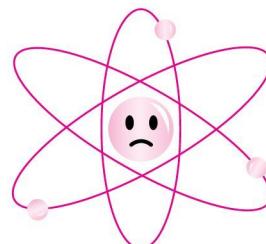
(b) Rate of reaction depends on the surface area. The total surface area of the wooden pieces is larger than the log of wood of the same mass. Greater the surface area, faster is the reaction.

(c) The slowest step of a complex reaction is the rate determining step.



CHEM CAPSULE

You should really care about atoms



THEY MATTER!

(d) A reaction intermediate is a molecular entity that is formed from the reactants but is consumed in further reactions in stepwise chemical reactions that contain multiple elementary steps. But transition state is a hypothetical complex, which is assumed to be formed in between the reactant and the product. Transition state has no real existence.

(e) Molecularity is the number of reacting species (molecules, atoms or ions) which collide simultaneously to bring about a chemical reaction.

(f) Yes

(g) Unimolecular, i.e., molecularity = 1

32. (i) The highly unstable transition state between reactants and products is called activated complex.



Energy of activation = Energy of activated complex
– Average energy of reactants.

(ii) Given that the rate of souring of milk at 20°C is three times as fast as at 3°C.

Therefore, $\frac{k_{(293\text{ K})}}{k_{(276\text{ K})}} = 3$,

$$\text{Since } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\text{or } E_a = \frac{2.303RT_1T_2}{(T_2 - T_1)} \log \frac{k_{293\text{ K}}}{k_{276\text{ K}}}$$

$$= \frac{2.303 \times 8.314 \times 10^{-3} \times 276 \times 293}{17} \log 3 = 43.46 \text{ kJ mol}^{-1}$$

OR

(i) Given : $k = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$, $n = 0$

$[R]_0 = 0.10 \text{ M}$, $[R] = 0.075 \text{ M}$

$$\text{Using formula, } t = \frac{[R]_0 - [R]}{k} = \frac{0.10 \text{ M} - 0.075 \text{ M}}{0.0030 \text{ mol L}^{-1} \text{ s}^{-1}}$$

$$t = \frac{0.025}{0.0030} = 8.3 \text{ s}$$

(ii) (a) For a first order reaction, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

Given $t = 15 \text{ min}$, $R = 0.8[R]_0$

$$\text{or, } k = \frac{2.303}{15} \log \frac{[R]_0}{0.8[R]_0} \text{ or, } k = \frac{2.303}{15} \log \frac{10}{8} \dots (\text{i})$$

or, $k = 0.015 \text{ min}^{-1}$

(b) When $[R] = 0.1 [R]_0$, $t = ?$

$$k = \frac{2.303}{t_1} \log \frac{[R]_0}{0.1[R]_0} = \frac{2.303}{t_1} \log 10 \dots (\text{ii})$$

$$\text{or, } 0.015 \text{ min}^{-1} = \frac{2.303}{t_1} \text{ or, } t_1 = \frac{2.303}{0.015 \text{ min}^{-1}}$$

$t_1 = 153.53 \text{ min}$

\therefore After 153.53 min, 10% of the original material remains unreacted.

$$(c) \text{Also, } k = \frac{2.303}{t_2} \log \frac{0.8[R]_0}{0.64[R]_0} = \frac{2.303}{t_2} \log \frac{10}{8} \dots (\text{iii})$$

From eq. (i) and eq. (iii),

$$\frac{2.303}{15} \log \frac{10}{8} = \frac{2.303}{t_2} \log \frac{10}{8} \therefore t_2 = 15 \text{ min}$$

33. (i) A reaction in which rate is independent of concentration of reactants is called zero order reaction. e.g., thermal decomposition of HI on gold surface.

(ii) The given rate law equation can be written as

$$-\frac{d[NH_3]}{dt} = \frac{k_1}{1/[NH_3] + k_2}$$

(a) If $[NH_3]$ is very high, $1/[NH_3]$ becomes negligible.

$$\therefore -\frac{d[NH_3]}{dt} = \frac{k_1}{k_2}$$

i.e., rate becomes independent of concentration. Hence, it is of zero order.

(b) If $[NH_3]$ is very small, $1/[NH_3]$ will be very large ($>>k_2$), so that k_2 can be neglected in comparison to $1/[NH_3]$. Hence $-\frac{d[NH_3]}{dt} = \frac{k_1}{1/[NH_3]} = k_1[NH_3]$

Thus, reaction is of 1st order.

OR

(i) The reactions which are of second order but behave like first order reactions are called pseudo first order reactions e.g., during hydrolysis of ethyl acetate (ester) with water, the concentration of water does not alter much during the reaction. So, in the rate equation, the rate of change in water concentration (the reactant which is in excess) can be taken as constant hence the reaction behaves as first order reaction.

$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$
Rate = $k'[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$ the term $[\text{H}_2\text{O}]$ can be taken as constant. Hence, the rate equation becomes

Rate = $k[\text{CH}_3\text{COOC}_2\text{H}_5]$ where $k = k'[\text{H}_2\text{O}]$.

(ii) Expression for rate constant of a zero order reaction is, $k = \frac{[R]_0 - [R]}{t}$

where $[R]_0$ is the initial concentration, $[R]$ is the final concentration and t is time.

k = proportionality constant called rate constant of reaction. Unit of rate constant of zero order reaction.

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

x and y are zero for zero order reaction.

$$\text{or } k = \text{mol L}^{-1} \text{ s}^{-1}$$



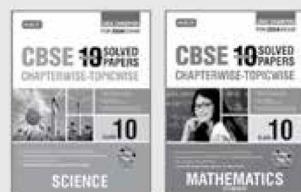
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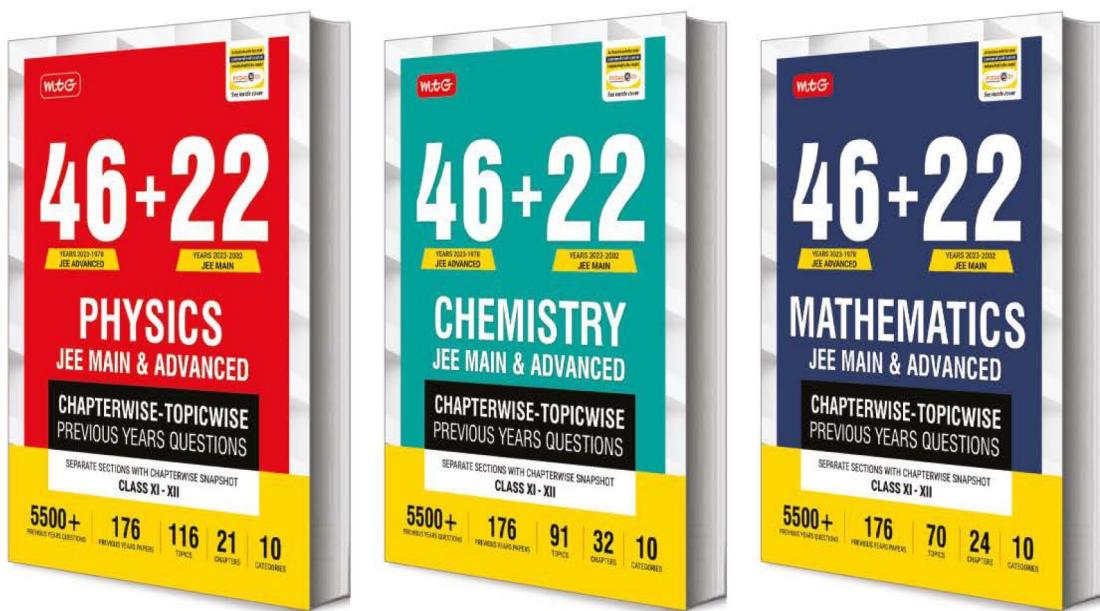
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