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ESSENTIALS

Class
XI

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Unit 2

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES CHEMICAL BONDING AND MOLECULAR STRUCTURE

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

HISTORY OF THE PERIODIC TABLE

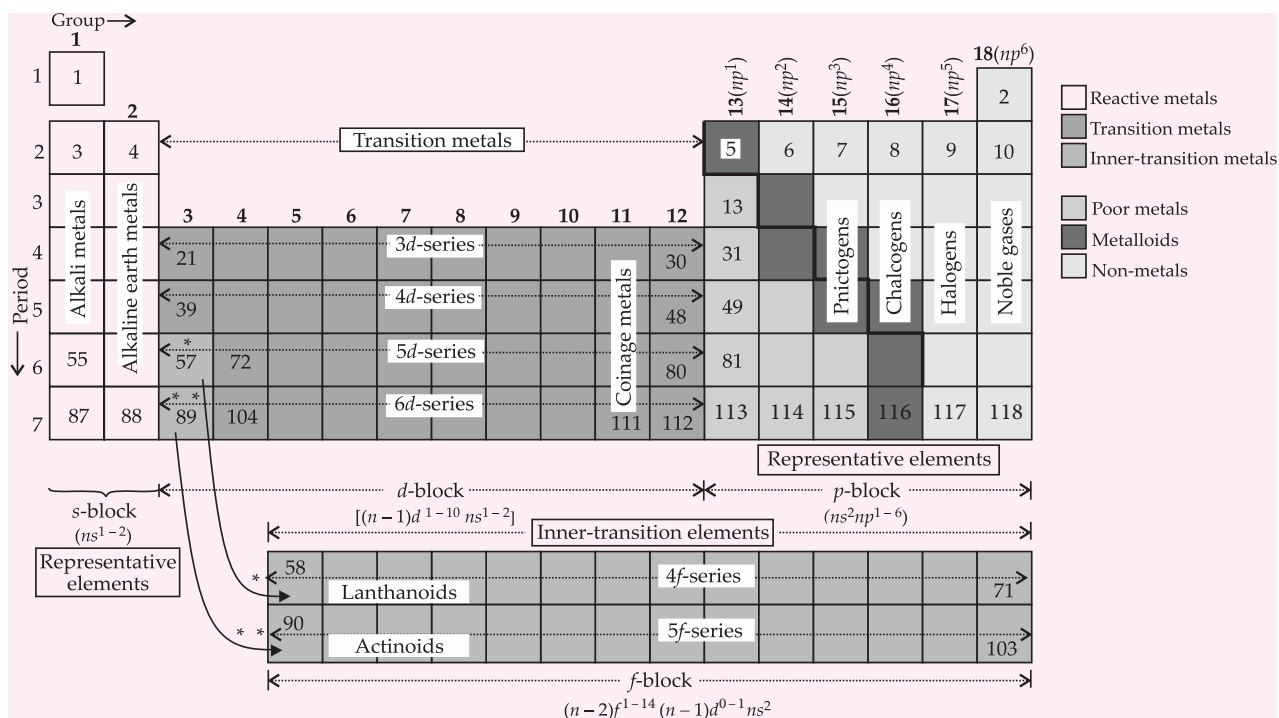
Earlier Attempts	Dobereiner's Triads	Mendeleev's Periodic Table	Newland's Law of Octaves
	In the triad of elements, the atomic weight of middle element is the arithmetic mean of other two.	Elements are arranged such that the properties of the elements are the periodic function of their atomic weights. This table contains 9 groups and 12 series (or 6 periods).	Elements are arranged in increasing order of their atomic weights, the properties of every eighth element are similar to the first one.

MODERN PERIODIC LAW

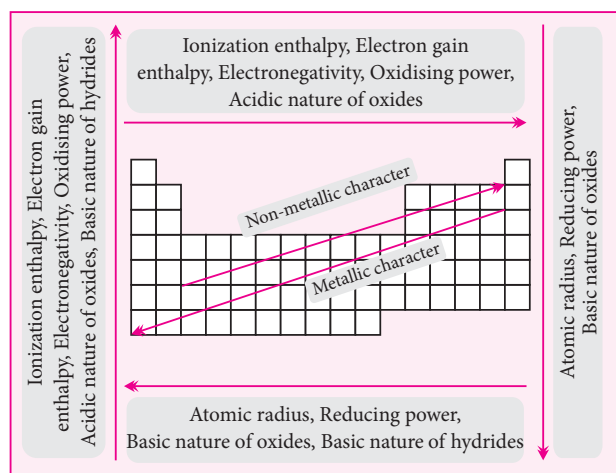
- ↪ The physical and chemical properties of elements are periodic functions of their atomic numbers.
- ↪ Periodic function is due to repetition of similar outer electronic configurations after certain regular intervals.

STRUCTURAL FEATURES OF PRESENT FORM OF THE PERIODIC TABLE

- ↪ The present form of periodic table consists of 18 vertical columns called groups and 7 horizontal rows called periods. Period number corresponds to the highest principal quantum number (n) of the elements.



PERIODIC TRENDS



ATOMIC RADIUS

- ↪ **Crystal or metallic radius** : It is one-half of the internuclear distance between the two nearest atoms in the metallic lattice. It is generally used for metals.
- ↪ **van der Waals radius** : It is one-half of the internuclear distance between the two adjacent identical atoms belonging to two neighbouring molecules of an element.

↪ **Covalent radius** : It is one-half of the distance between the centres of the nuclei of two similar atoms joined by a single covalent bond. This is generally used for non-metals.

- The atomic radii of noble gases or inert gases are, in fact, van der Waals radii since they do not form molecules.
- van der Waals radius > metallic radius > covalent radius (for an atom)

IONIC RADIUS

↪ Cation is smaller and anion is larger than the parent atom of the element. In case of isoelectronic ions, the size decreases with increase in the nuclear charge.

IONISATION ENTHALPY

$$I.E. \propto \frac{1}{\text{size of atom}} \propto \text{Effective nuclear charge}$$

$$\propto \frac{1}{\text{Screening effect}}$$

↪ Completely or half-filled orbital has higher *I.E.* because of higher stability.

ELECTRON GAIN ENTHALPY

$$\Delta_{eg}H \propto \frac{1}{\text{Size of atom}} \propto \frac{\text{Effective nuclear charge}}{1} \propto \frac{1}{\text{Screening effect}}$$

ELECTRONEGATIVITY

↪ Mulliken scale of electronegativity

$$\chi = \frac{1}{2} [\Delta_i H + \Delta_{eg} H]$$

↪ Pauling scale of electronegativity

$$\chi_A - \chi_B = 0.1017 \sqrt{\Delta}$$

$$\text{where, } \Delta = E_{A-B} - \frac{1}{2} \sqrt{E_{A-A} + E_{B-B}}$$

Here, E represents bond dissociation enthalpy (in kJ mol^{-1}).

↪ Percentage ionic character

$$= 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$$

- If $\chi_A - \chi_B = 1.7$, bond is 50% covalent and 50% ionic.
- If $\chi_A - \chi_B > 1.7$, bond is predominately ionic.
- If $\chi_A \approx \chi_B$, $A - B$ bond is purely covalent.

INFOSHOTS

Four new elements now have names!

In December 2015, the International Union of Pure and Applied Chemistry officially recognized the discovery of elements 113, 115, 117 and 118, filling out the seventh row of the periodic table. Element 113 is dubbed “nihonium” and will sport the chemical symbol Nh. Its name comes from the Japanese word “Nihon”. Element 115 will receive the moniker “moscovium,” shortened to Mc, after the Moscow region. The proposed name for element 117 is “tennessine,” having symbol Ts, after the home state of Oak Ridge, Vanderbilt University and the University of Tennessee. Element 118 will be named oganesson, or Og, after Russian physicist Yuri Oganessian.

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Types of Bonds

☐ Covalent Bond

Bond formed by mutual sharing of electrons between the atoms.

☐ Coordinate Bond

A special type of covalent bond where shared pair of electrons is donated by one atom to other.

☐ Ionic Bond

Bond formed by transferring of valence electrons from one atom to another.

Conditions Required :

- ↪ Electronegativity difference between the atoms must be high.
- ↪ Low ionisation energy of the element forming cation and high electron affinity of the element forming anion.
- ↪ Lattice energy for formation of ionic compound must be high.

$$\Delta H_f = \Delta H_s + IE + \frac{1}{2} \Delta H_d - EA - U$$

where ΔH_f = Enthalpy of formation,

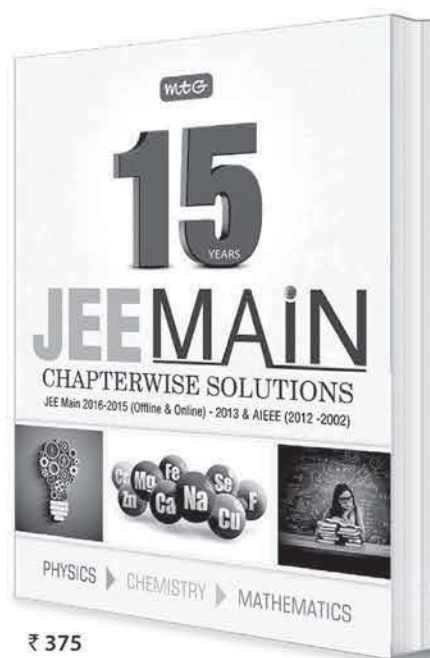
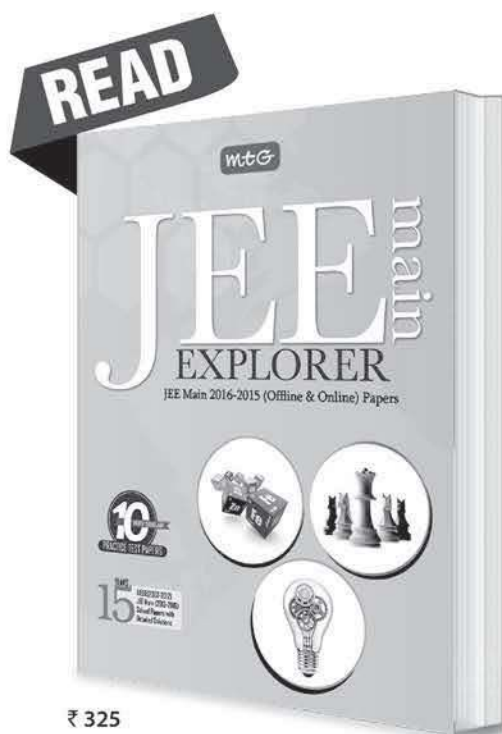
ΔH_s = Enthalpy of sublimation,

IE = Ionisation energy,

ΔH_d = Enthalpy of dissociation,

EA = Electron affinity and U = Lattice energy.

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FAJAN'S RULE

The magnitude of covalent character in the ionic bond depends upon the extent of polarization caused by cation.

- Smaller the cation, larger is its polarizing power.
- Larger the anion, more is its polarisability.

VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

- The best arrangement of a given number of electron pairs is the one that minimises the repulsion among them.
- Repulsive interactions** : Lone pair - lone pair > lone pair - bond pair > bond pair - bond pair
- Valence bond theory (VBT)** : The formation of a covalent bond is due to pairing of electrons present in the valence shell having opposite spins. Head on overlap of atomic orbitals gives σ bond, sideway overlap of atomic orbitals gives π bond.

HYBRIDISATION

- It is the process of intermixing of orbitals with slightly different energies so as to redistribute their energies giving another set of orbitals (called *hybrid orbitals*) with same energy, size and shape.
- The structure of any molecule can be predicted on the basis of hybridisation by formula :
No. of hybrid orbitals (H)

$$= \frac{1}{2} \left[\left(\text{No. of valence electrons of central atom} \right) + \left(\text{No. of monovalent atoms} \right) - \left(\text{Charge present on the cation} \right) + \left(\text{Charge present on the anion} \right) \right]$$

$$\Rightarrow H = \frac{1}{2} [V + M - C + A]$$

Types of Hybridization	Orbitals mixed	Shape of the molecule/ion	Examples
sp	one s + one p	Linear	$\text{BeF}_2, \text{BeH}_2, \text{C}_2\text{H}_2, \text{HgCl}_2$
sp^2	one s + two p	Triangular planar	$\text{BF}_3, \text{C}_2\text{H}_4, \text{NO}_3^-, \text{CO}_3^{2-}$
sp^3	one s + three p	Tetrahedral	$\text{CH}_4, \text{CCl}_4, \text{SnCl}_4, \text{NH}_4^+, [\text{Ni}(\text{CO})_4]$
dsp^2	one $d(d_{x^2-y^2})$ + one s + two p	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}, [\text{PtCl}_4]^{2-}$
sp^3d	one s + three p + one $d(d_{z^2})$	Trigonal bipyramidal	$\text{PF}_5, \text{PCl}_5$
sp^3d^2	one s + three p + two $d(d_{x^2-y^2}, d_{z^2})$	Octahedral	$\text{SF}_6, [\text{CrF}_6]^{3-}, [\text{Co}(\text{NH}_3)_6]^{3+}$
sp^3d^3	one s + three p + three $d(d_{xy}, d_{yz}, d_{xz})$	Pentagonal bipyramidal	IF_7

MOLECULAR ORBITAL THEORY

- The atomic orbitals of comparable energy and proper symmetry combine to form equal number of molecular orbitals.
- The *bonding molecular orbital* has lower energy and greater stability than the corresponding *anti-bonding molecular orbital*.

- The order of energies of molecular orbitals for simple homonuclear diatomic molecules like O_2, F_2 and Ne_2 is $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \pi 2p_x = \pi 2p_y, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$
- The order of energies of molecular orbitals for diatomic lighter elements like B_2, C_2 and N_2 is $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \pi 2p_x = \pi 2p_y, \sigma 2p_z, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$

- ↪ Bond order = $\frac{1}{2}(N_b - N_a)$
 [N_b = No. of bonding electrons, N_a = No. of antibonding electrons]

HYDROGEN BONDING

- ↪ The attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule is called

hydrogen bond.

It can be intermolecular (in case of HF, ROH or H₂O) or intramolecular (in case of *o*-nitrophenol).

METALLIC BONDING

- ↪ Metallic bond is electrostatic force of attraction between positively charged kernels (nuclei with core electron) and mobile electrons which holds the metal atoms together.



New type of chemical bond confirmed!

Chemists in 1989, experimenting at a nuclear accelerator in Vancouver observed that a reaction between bromine and muonium (a hydrogen isotope) slowed down when they increased the temperature. However, the rate of a reaction should speed up as temperature rises. Then chemists thought that bromine and muonium formed an intermediate structure held together by a “vibrational” bond—a bond that other chemists had posed as a theoretical possibility earlier that decade. The lightweight muonium atom would move rapidly between two heavy bromine atoms, “like a Ping Pong ball bouncing between two bowling balls”. Now, they concluded that muonium and bromine were indeed forming a new type of temporary bond. Its vibrational nature lowered the total energy of the intermediate bromine-muonium structure.

SPEED PRACTICE

- In the series of ethane, ethylene and acetylene, the C—H bond energy is
 - the same in all the three compounds
 - greatest in ethane
 - greatest in ethylene
 - greatest in acetylene.
- The species in which the N atom is in a state of *sp* hybridisation is

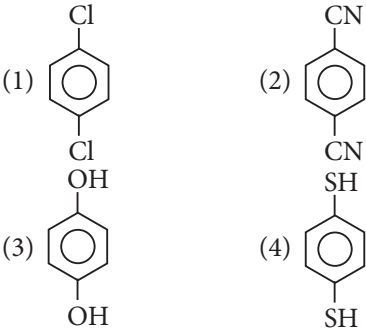
(a) NO ₂ ⁺	(b) NO ₂ ⁻
(c) NO ₃ ⁻	(d) NO ₂ (JEE Main 2016)
- In PO₄³⁻ ion, the formal charge on each oxygen atom and bond order of P—O bond are respectively

(a) -0.75, 1.25	(b) -0.75, 1.0
(c) -0.75, 0.6	(d) -3, 1.25
- Assuming *2s-2p* mixing is not operative, the paramagnetic species among the following is

(a) Be ₂	(b) B ₂
(c) C ₂	(d) N ₂

(JEE Advanced 2014)
- The ionic species having largest size is

(a) Li _(g) ⁺	(b) Na _(aq) ⁺
(c) Rb _(aq) ⁺	(d) Li _(aq) ⁺
- Consider the molecules CH₄, NH₃ and H₂O. Which of the given statements is false?
 - The H—O—H bond angle in H₂O is smaller than the H—N—H bond angle in NH₃.
 - The H—C—H bond angle in CH₄ is larger than the H—N—H bond angle in NH₃.
 - The H—C—H bond angle in CH₄, the H—N—H bond angle in NH₃, and the H—O—H bond angle in H₂O are all greater than 90°.

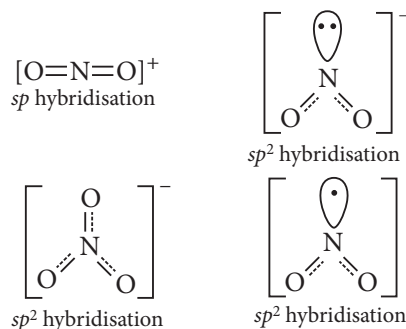
- (d) The H—O—H bond angle in H₂O is larger than the H—C—H bond angle in CH₄.
(NEET 2016)
7. Which one of the following is incorrect?
(a) An element which has high electronegativity always has high electron gain enthalpy.
(b) Electron gain enthalpy is the property of an isolated atom.
(c) Electronegativity is the property of a bonded atom.
(d) Both electronegativity and electron gain enthalpy are usually directly related to nuclear charge and inversely related to atomic size.
8. Maximum bond angle at nitrogen is present in which of the following?
(a) NO₂⁺ (b) NO₃⁻
(c) NO₂ (d) NO₂⁻ (AIPMT 2015)
9. The ionic radii (in Å) of N³⁻, O²⁻ and F⁻ are respectively
(a) 1.71, 1.40 and 1.36 (b) 1.71, 1.36 and 1.40
(c) 1.36, 1.40 and 1.71 (d) 1.36, 1.71 and 1.40
(JEE Main 2015)
10. Which transition involves maximum amount of energy?
(a) $M_{(g)}^- \longrightarrow M_{(g)} + e^-$ (b) $M_{(g)}^- \longrightarrow M_{(g)}^+ + 2e^-$
(c) $M_{(g)}^+ \longrightarrow M_{(g)}^{2+} + e^-$ (d) $M_{(g)}^{2+} \longrightarrow M_{(g)}^{3+} + e^-$
11. Which one of the following species has plane triangular shape?
(a) N₃ (b) NO₃⁻
(c) NO₂⁻ (d) CO₂ (AIPMT 2014)
12. Predict the correct order of repulsion among the following :
(a) bond pair - bond pair > lone pair - bond pair > lone pair - lone pair
(b) lone pair - bond pair > bond pair - bond pair > lone pair - lone pair
(c) lone pair - lone pair > lone pair - bond pair > bond pair - bond pair
(d) lone pair - lone pair > bond pair - bond pair > lone pair - bond pair
(NEET 2016)
13. Which of the following molecules is theoretically not possible?
(a) OF₄ (b) SF₄
(c) OF₂ (d) O₂F₂
14. Which of the following compounds doesn't have linear structure?
(a) CO₂ (b) SO₂
(c) BeCl₂ (d) C₂H₂
15. For which of the following molecules significant $\mu \neq 0$?

(a) (3) and (4) (b) Only (1)
(c) (1) and (2) (d) Only (3)
(JEE Main 2014)
16. The elements which exhibit both vertical and horizontal similarities are
(a) noble gas
(b) representative elements
(c) transition elements
(d) rare earth elements.
17. Which one has the highest boiling point?
(a) Kr (b) Xe
(c) He (d) Ne (JEE Main 2015)
18. The strength of an oxyacid E(OH)_n, where E is the central atom, depends upon
(a) electronegativity of E but not on oxidation state of E
(b) atomic size of E but not on electronegativity of E
(c) not on oxidation state of E in oxyacids
(d) atomic size, electronegativity and oxidation state of E.
19. Which of the following pairs of ions are isoelectronic and isostructural?
(a) SO₃²⁻, NO₃⁻ (b) ClO₃⁻, SO₃²⁻
(c) CO₃²⁻, SO₃²⁻ (d) ClO₃⁻, CO₃²⁻
(AIPMT 2015)
20. In which of the following options the order of arrangement does not agree with the variation of property indicated against it?
(a) I < Br < Cl < F (increasing electron gain enthalpy)

- (b) $\text{Li} < \text{Na} < \text{K} < \text{Rb}$ (increasing metallic radius)
 (c) $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$ (increasing ionic size)
 (d) $\text{B} < \text{C} < \text{N} < \text{O}$ (increasing first ionisation enthalpy) (NEET 2016)
21. According to molecular orbital theory which of the following statements about the magnetic character and bond order is correct regarding O_2^+ ?
 (a) Paramagnetic and bond order $< \text{O}_2$
 (b) Paramagnetic and bond order $> \text{O}_2$
 (c) Diamagnetic and bond order $< \text{O}_2$
 (d) Diamagnetic and bond order $> \text{O}_2$
22. Which of the following molecules has the maximum dipole moment?
 (a) CO_2 (b) CH_4
 (c) NH_3 (d) NF_3 (AIPMT 2014)
23. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is
 (a) London force
 (b) hydrogen bond
 (c) ion-ion interaction
 (d) ion-dipole interaction. (JEE Main 2015)
24. Most efficient overlapping is
 (a) sp^2 - sp^2 overlap (b) s - s overlap
 (c) sp^3 - sp^3 overlap (d) sp - sp overlap.
25. The shape of XeOF_2 on the basis of VSEPR theory is
 (a) see saw (b) V-shaped
 (c) trigonal planar (d) T-shaped.
26. The correct statement for the molecule, CsI_3 , is
 (a) it contains Cs^+ , I^- and lattice I_2 molecule
 (b) it is a covalent molecule
 (c) it contains Cs^+ and I_3^- ions
 (d) it contains Cs^{3+} and I^- ions. (JEE Main 2014)
27. In which one of the following pairs the radius of the second species is greater than that of the first?
 (a) Na , Mg (b) O^{2-} , N^{3-}
 (c) Li^+ , Be^{2+} (d) Ba^{2+} , Sr^{2+}
28. The species Ar , K^+ and Ca^{2+} contain the same number of electrons. In which order do their radii increase?
 (a) $\text{Ca}^{2+} < \text{K}^+ < \text{Ar}$ (b) $\text{K}^+ < \text{Ar} < \text{Ca}^{2+}$
 (c) $\text{Ar} < \text{K}^+ < \text{Ca}^{2+}$ (d) $\text{Ca}^{2+} < \text{Ar} < \text{K}^+$
 (AIPMT 2015)
29. If x -axis is the molecular axis, then π -molecular orbitals are formed by the overlap of
 (a) $s + p_z$ (b) $p_x + p_y$
 (c) $p_z + p_z$ (d) $p_x + p_x$
30. Which of the following represents the correct order of increasing first ionization enthalpy for Ca , Ba , S , Se and Ar ?
 (a) $\text{Ca} < \text{Ba} < \text{S} < \text{Se} < \text{Ar}$
 (b) $\text{Ca} < \text{S} < \text{Ba} < \text{Se} < \text{Ar}$
 (c) $\text{S} < \text{Se} < \text{Ca} < \text{Ba} < \text{Ar}$
 (d) $\text{Ba} < \text{Ca} < \text{Se} < \text{S} < \text{Ar}$

SOLUTIONS

1. (d): As the bond order increases, C—H bond energy also increases so it will be greatest in acetylene because bond order of ethane, ethylene and acetylene is 1, 2 and 3 respectively.

2. (a):



3. (a): Formal charge on an atom = No. of valence electrons - total no. of electrons of lone pairs - $\frac{1}{2}$ [no. of shared electrons]

Thus, for PO_4^{3-} ions, 3 single bonded oxygen atoms have formal charge = -1 and double bonded oxygen has formal charge = 0.

$$\text{Formal charge on O atoms} = \frac{-3}{4} = -0.75$$

$$\text{P—O bond order} = \frac{5}{4} = 1.25$$

(5 bonds between 4 oxygen atoms)

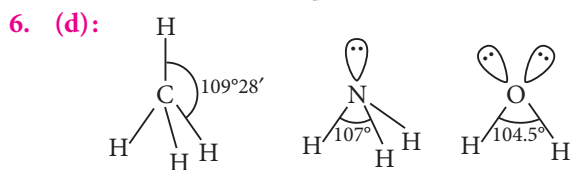
4. (c): If $2s$ - $2p$ mixing is not operative, then molecular orbitals may be arranged in order of energy as follows:

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \pi 2p_x = \pi 2p_y, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$$

Applying this configuration, Be_2 , B_2 and N_2 will be diamagnetic, but C_2 will be paramagnetic with electronic configuration:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^1 = \pi 2p_y^1$$

5. (d): $\text{Li}^+_{(g)}$ ion being smallest in size is heavily hydrated and thus, $\text{Li}^+_{(aq)}$ is largest in size.



Two lone pairs of electrons in H_2O cause more repulsion to suppress the $\text{H}-\text{O}-\text{H}$ bond angle more than in NH_3 (one lone pair of electrons). While in CH_4 there is no lone pair of electrons hence, it has normal tetrahedral bond angles.

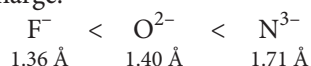
7. (a): Elements with high electronegativity usually but not always have high negative electron gain enthalpies. e.g., both N and Cl have an electronegativity of 3.0 but the electron gain enthalpy of N is positive while that of chlorine is the highest with negative sign in the periodic table.

8. (a):

Species	NO_2^+	NO_3^-	NO_2	NO_2^-
Hybridisation	sp (linear)	sp^2	sp^2	sp^2
Bond angle	180°	120°	134°	115°

So, NO_2^+ has maximum bond angle.

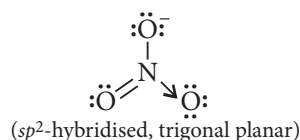
9. (a): The ionic radii of isoelectronic ions increase with the decrease in magnitude of the nuclear charge.



10. (d): When an electron is removed from an isolated gaseous atom it forms a cation in which electrons become less but nuclear charge remains same thus, the electrons are more tightly bounded in cations. Hence, energy required to pull out these electrons is higher.

$$IE_3 > IE_2 > IE_1$$

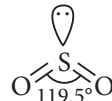
11. (b):



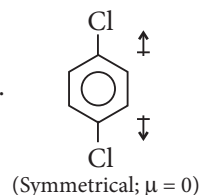
12. (c): The bond pair of electrons are shared between two atoms but lone pair of electrons are localised on the atom thus, occupies more space and causes greater repulsion. Thus, order of repulsion is lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

13. (a): Oxygen does not contain d -orbitals in its valence shell and hence cannot extend its coordination number. Hence, oxygen cannot accommodate four fluorine atoms to form OF_4 .

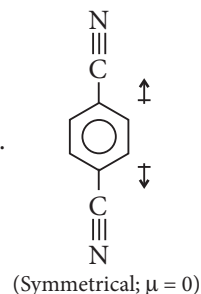
14. (b): SO_2 molecule shows sp^2 -hybridisation and has bent structure.



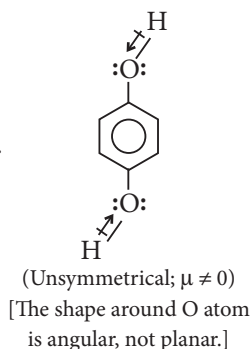
15. (a): 1.



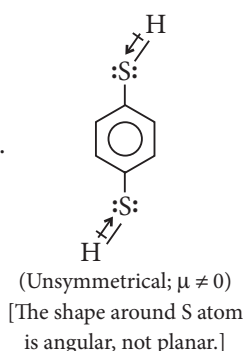
2.



3.



4.



16. (c): Transition elements due to same number of valence electrons in outermost shell i.e., ns^2 show both vertical and horizontal similarities.

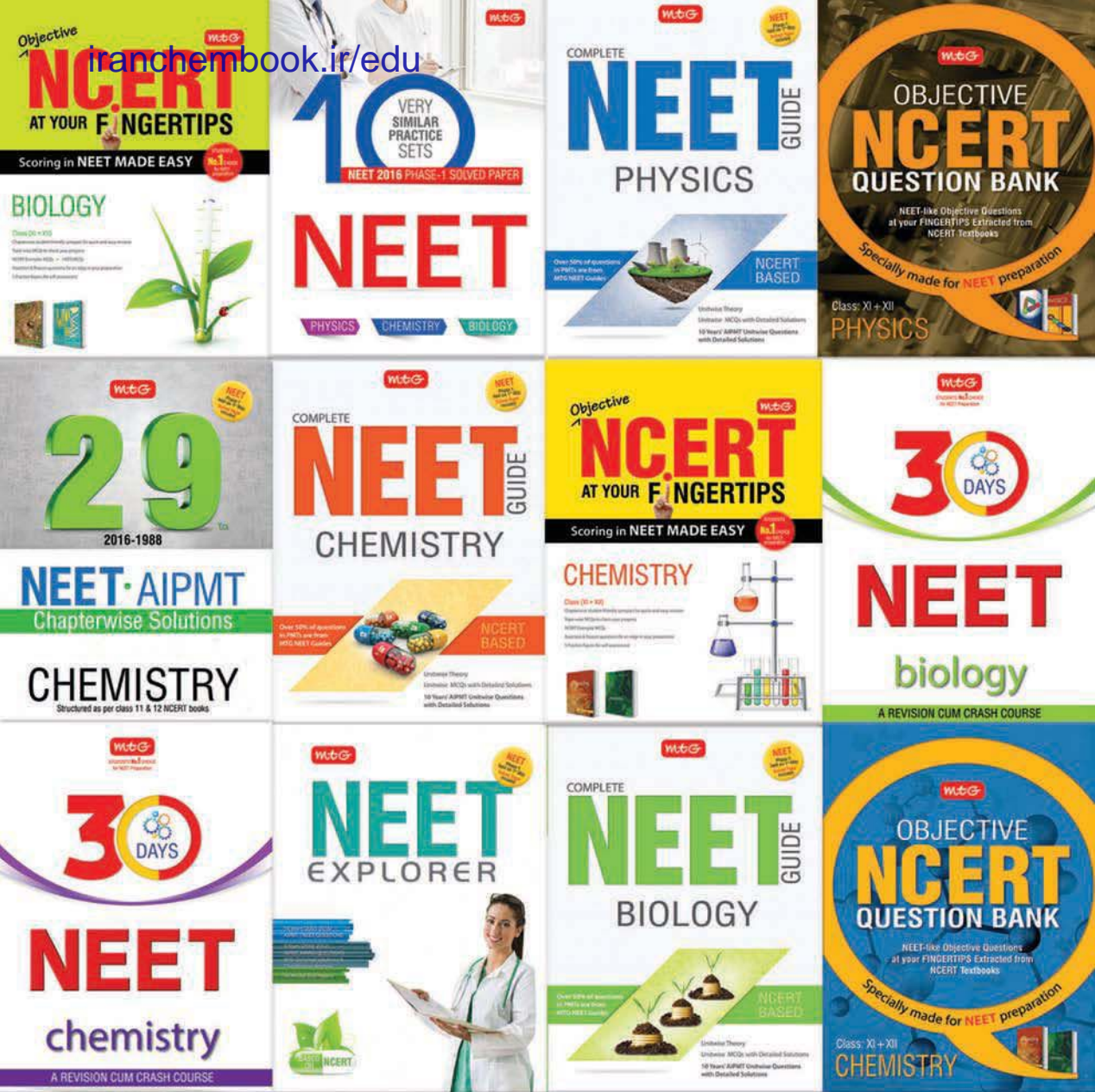
17. (b): Boiling point increases down the group from He to Rn due to increase in van der Waals' forces of attraction as the size of the atom increases.

18. (d)

19. (b):

Species	Hybridisation	Shape	No. of e^- s
SO_3^{2-}	sp^3	Pyramidal	42
ClO_3^-	sp^3	Pyramidal	42
CO_3^{2-}	sp^2	Triangular planar	32
NO_3^-	sp^2	Triangular planar	32

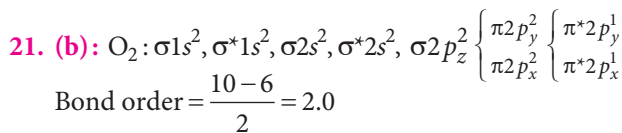
20. (a,d): In fluorine, due to its small size incoming electron will experience more repulsion from the valence electrons thus, it has lower negative electron



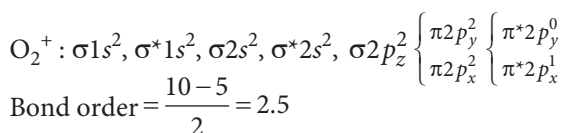
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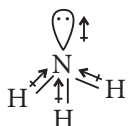
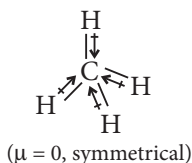
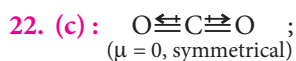
gain enthalpy than chlorine. The correct order of increasing negative electron gain enthalpy is : $I < Br < F < Cl$ and the correct order of increasing first ionisation enthalpy is $B < C < O < N$ due to half filled orbital of nitrogen which provides extra stability to valence electrons of nitrogen.



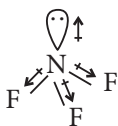
Two unpaired electrons in antibonding molecular orbital.



One unpaired electron in antibonding molecular orbital so it is paramagnetic.



($\mu \neq 0$, pyramidal)



($\mu \neq 0$, pyramidal)

In NH_3 , H is less electronegative than N and hence dipole moment of each N—H bond is towards N and create high net dipole moment whereas in NF_3 , F is more electronegative than N, the dipole moment of each N—F bond is opposite to that of lone pair hence, reducing the net dipole moment.

23. (b): Dipole-dipole interaction (hydrogen bonding) is proportional to $1/r^3$, where r is the distance between the polar molecules.

24. (d): Overlapping is better in hybrid orbitals due to same size and equivalent energy than the pure orbitals. Among hybrid orbitals, more is the s character greater is the strength of bond.

25. (d): $XeOF_2$

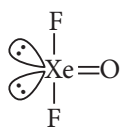
π bond = 1

Total number of electron pairs = 6

Number of lone pairs = 2

Shape \longrightarrow T-shaped geometry

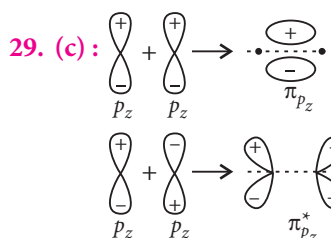
Hybridization $\longrightarrow sp^3d$



26. (c): Cs cannot show +3 oxidation state. So, CsI_3 is formulated as Cs^+ and I_3^- ions. It is a typical ionic compound.

27. (b): N^{3-} and O^{2-} both are isoelectronic but differ in the charge possessed by them. As the nuclear charge decreases from O to N, the electrons are held less and less tightly by the nucleus. Hence, the ionic size increases from O^{2-} to N^{3-} .

28. (a): In case of isoelectronic species, radius decreases with increase in nuclear charge.



30. (d): Ionization enthalpy increases on moving from left to right across the period as the size decreases and decreases on moving top to bottom in a group as the size increases. Ar has the maximum value of $I.E.$, since it is a noble gas. So, the correct order of increasing first ionization enthalpy ($\Delta_i H_1$) is

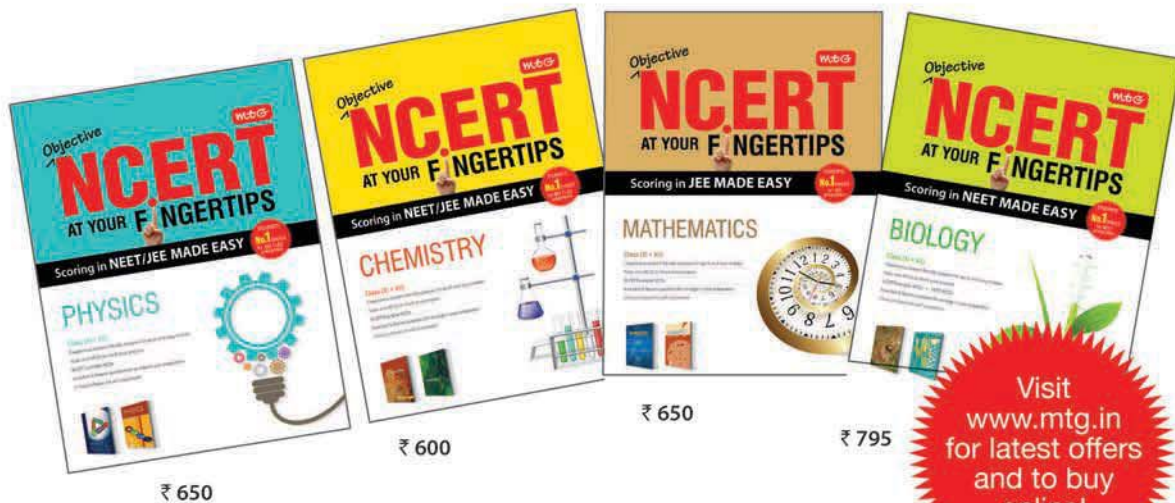
$Ba < Ca < Se < S < Ar$.

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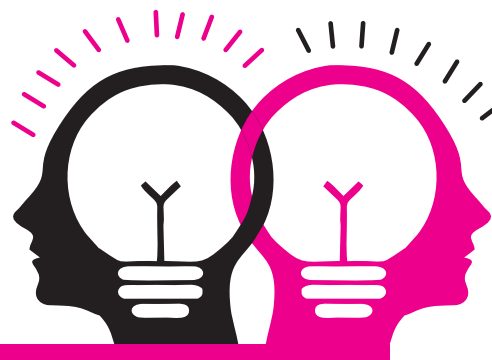


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EXAMINER'S MIND CLASS XI



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

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

STRUCTURE OF ATOM

SECTION - I

Only One Option Correct Type

- Which of the following is never true for cathode rays?
 - They possess kinetic energy.
 - They are electromagnetic waves.
 - They produce heat.
 - They produce mechanical pressure.
- The near UV photon of 300 nm is absorbed by a gas and then re-emitted as two photons. One photon is red with the wavelength 760 nm. Hence, wavelength of the second photon is

(a) 460 nm	(b) 1060 nm
(c) 496 nm	(d) 300 nm
- Photoelectric effect is the phenomenon in which
 - photons come out the metal when hit by a beam of electrons
 - photons come out of the nucleus of an atom under the action of an electric field
 - electrons come out of metal with a constant velocity which depends on frequency and intensity of incident light
 - electrons come out of metal with different velocities not greater than a certain value which depends upon frequency of incident light and not on intensity.
- When a certain metal was irradiated with light of frequency 3.2×10^{16} Hz, photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency 2.0×10^{16} Hz. Hence, threshold frequency is
 - 0.8×10^{15} Hz
 - 8.0×10^{15} Hz
 - 0.85×10^{14} Hz
 - 6.4×10^{16} Hz
- The nucleus of an atom can be assumed to be spherical. The radius of the nucleus of mass number A is given by $1.25 \times 10^{-13} \times A^{1/3}$ cm. Radius of atom is one Å. If the mass number is 64, then the fraction of the atomic volume that is occupied by the nucleus is

(a) 1.0×10^{-3}	(b) 5.0×10^{-5}
(c) 2.5×10^{-2}	(d) 1.25×10^{-13}

6. If azimuthal quantum number could have value of n also (in addition of normal value), then electronic configuration of V ($Z = 23$) would have been
- (a) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
 (b) $1s^2, 1p^6, 2s^2, 2p^6, 2d^7$
 (c) $1s^2, 1p^6, 2s^2, 2p^6, 3s^2, 2d^5$
 (d) $1s^2, 1p^6, 2s^2, 2p^6, 3s^1, 2d^6$

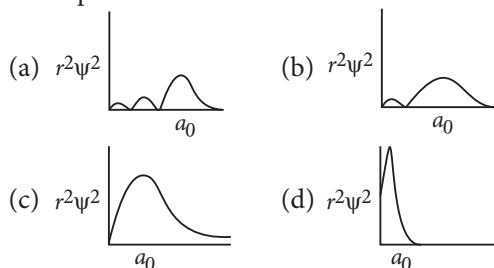
7. Which of the following electronic configurations has zero spin multiplicity?



8. If the shortest wavelength of H atom in Lyman series is x , then longest wavelength in Balmer series of He^+ is

(a) $\frac{9x}{5}$ (b) $\frac{36x}{5}$ (c) $\frac{x}{4}$ (d) $\frac{5x}{9}$

9. Which of the following radial distribution graphs corresponds to $l = 2$ for the H atom?



10. The ratio of the energy of the electron in ground state of hydrogen to the electron in first excited state of Be^{3+} is

(a) 1 : 4 (b) 1 : 8
 (c) 1 : 16 (d) 16 : 1

SECTION - II

More than One Options Correct Type

11. Which of the following is/are not correct?
- (a) Isotones differ in the number of neutrons.
 (b) Isobars contain the same number of neutrons but differ in the number of protons.
 (c) No isotope of hydrogen is radioactive.
 (d) Density of nucleus is much greater than that of atom.
12. Which of the following sets of quantum number is/are not allowed?
- (a) $n = 3, l = 2, m = -1$ (b) $n = 2, l = 3, m = -1$
 (c) $n = 3, l = 0, m = 1$ (d) $n = 6, l = 2, m = -1$

13. Out of the following pairs of electrons, identify the pairs of electrons present in degenerate orbitals :

- (a) (i) $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$
 (ii) $n = 3, l = 2, m_l = -1, m_s = -\frac{1}{2}$
 (b) (i) $n = 3, l = 1, m_l = 1, m_s = +\frac{1}{2}$
 (ii) $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$
 (c) (i) $n = 4, l = 1, m_l = 1, m_s = +\frac{1}{2}$
 (ii) $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$
 (d) (i) $n = 3, l = 2, m_l = +2, m_s = -\frac{1}{2}$
 (ii) $n = 3, l = 2, m_l = +2, m_s = +\frac{1}{2}$

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

The behaviour of an electron in an atom is described mathematically by a wave function, or orbital. It turns out that each wave function contains three variables, called quantum numbers, which are represented as n, l and m_l . These quantum numbers describe the energy level of an orbital and define the shape and orientation of the region in space where the electron will be found.

14. Which quantum number determines orientation of the electron?

- (a) Principal (b) Secondary
 (c) Magnetic (d) Spin

15. Radial nodes are maximum in

- (a) 4s (b) 4p (c) 3d (d) 5f

Paragraph for Questions 16 and 17

To explain the nature of radiations, James Clark Maxwell in 1864 put forward 'Electromagnetic wave theory'. This theory could explain the phenomenon of interference and diffraction but could not explain phenomena of black body radiation and photoelectric effect. Also, after the advent of electromagnetic wave theory, Rutherford's model of atom suffered a serious drawback. To explain the phenomenon of black body radiation and photoelectric effect, Max Planck in 1900 put forward Planck's quantum theory. Based

on this theory, Neil Bohr in 1913 put forward Bohr's model of atom which could overcome the drawback of Rutherford's model and also explain the line spectra of elements, especially the line spectra of hydrogen and hydrogen-like particles.

16. Which one of the following statements is incorrect about electromagnetic wave theory?
- Energy is emitted continuously from the source.
 - Radiations are associated with electric and magnetic fields.
 - Radiations can travel even through vacuum.
 - The velocity of any radiation depends upon the nature of the radiation.
17. The radiation having the largest wavelength is
- gamma-rays
 - microwaves
 - radiowaves
 - all of these have equal wavelength.

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the code given below the lists :

List I (Observation of scattering expt.)	List II (Conclusion drawn)
P. Some α -particles were deflected back after striking thin foil of gold.	1. There is a positively charged body within the atom.
Q. Some α -particles were deflected through small angles.	2. The positively charged body is quite heavy.
R. Most of the α -particles passed through the foil without undergoing any deflection.	3. The positively charged body occupies a very small volume.
S. The number of α -particles deflected back was very small.	4. There is sufficient empty space within the atom.

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

19. If the shortest wavelength of spectral line of H-atom in Lyman series is x , then match the following for Li^{2+} .

List I	List II
P. Shortest wavelength in Lyman series	1. $\frac{4x}{5}$
Q. Longest wavelength in Lyman series	2. $\frac{4x}{9}$
R. Shortest wavelength in Balmer series	3. $\frac{x}{9}$
S. Longest wavelength in Balmer series	4. $\frac{4x}{27}$

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

SECTION - V

Assertion Reason Type

20. **Assertion :** Bohr's orbits are called stationary orbits.
Reason : Electrons remain stationary in these orbits for some time.
21. **Assertion :** Angular momentum of an electron in any orbit = $\frac{n.h}{2\pi}$, where n is the principal quantum number.
Reason : The principal quantum number, n , can have any integral value.
22. **Assertion :** If the potential applied on the electron is quadrupled, the de-Broglie wavelength associated with the electron is halved.
Reason : If the potential applied on the electron is quadrupled, velocity is doubled and hence λ is halved.

SECTION - VI

Integer Value Correct Type

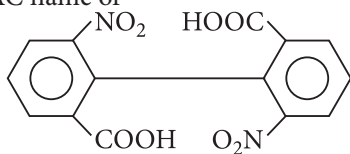
23. The number of waves by a Bohr electron in one complete revolution in its 3rd orbit is
24. A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. The uncertainty involved in the measurement of velocity is $5.79 \times 10^x \text{ m s}^{-1}$. The value of x is
25. An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than the electrons. The number of electrons in the neutral atom is $(5a + 1)$. The value of a is

ORGANIC CHEMISTRY : SOME BASIC PRINCIPLES AND TECHNIQUES

SECTION - I

Only One Option Correct Type

1. The IUPAC name of



- (a) 2, 2'-dinitrodiphenic acid
 (b) 6, 6'-dinitrodiphenic acid
 (c) 6, 6'-dinitrophenyl-2, 2'-dicarboxylic acid
 (d) 2, 2'-dinitrophenyl-6, 6'-dicarboxylic acid

2. A compound with molecular formula C_4H_4O has all the four carbon atoms and the oxygen atom in the ring. It also has two double bonds. The compound is

- (a) homocyclic and aromatic
 (b) heterocyclic and aromatic
 (c) homocyclic but not aromatic
 (d) heterocyclic but not aromatic.

3. Which of the following is the strongest nucleophile?

- (a) $CH_3-CH_2^-$ (b) $HC\equiv C^-$
 (c) NH_2^- (d) $H_2C=CH^-$

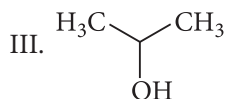
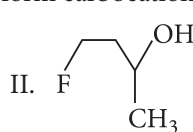
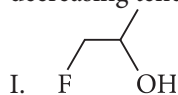
4. Which of the following is more appropriate representation for the resonance hybrid of nitrate ion?

- (a) $O=\ddot{N}^+ \begin{matrix} \diagup O^- \\ \diagdown O^- \end{matrix}$ (b) $^{-2/3}O \begin{matrix} \diagup O^- \\ \diagdown O^- \end{matrix} N^+$
 (c) $\left[O=\ddot{N}^+ \begin{matrix} \diagup O^- \\ \diagdown O^- \end{matrix} \right]$ (d) $\left[O-\ddot{N}^+ \begin{matrix} \diagup O^- \\ \diagdown O^- \end{matrix} \right]^{-2/3}$

5. The ascending order of stability of the carbanion $CH_3^-(P)$, $C_6H_5CH_2^-(Q)$, $(CH_3)_2CH^-(R)$ and $CH_2=CHCH_2^-(S)$ is

- (a) $P < R < S < Q$ (b) $R < P < S < Q$
 (c) $R < P < Q < S$ (d) $P < R < Q < S$

6. Arrange the following alcohols in order of their decreasing tendency to form carbocation.



- (a) $I > II > III > IV$ (b) $IV > III > I > II$
 (c) $IV > III > II > I$ (d) $II > I > IV > III$

7. Mark the incorrect statement for Kjeldahl's method of estimation of nitrogen.

- (a) Nitrogen gas is collected over caustic potash solution.
 (b) Potassium sulphate is used as boiling point elevator of H_2SO_4 .
 (c) Copper sulphate or mercury acts as a catalyst.
 (d) Nitrogen is quantitatively decomposed to give ammonium sulphate.

8. 0.22 g of organic compound C_xH_yO which occupied 112 mL at NTP and on combustion gave 0.44 g CO_2 . The ratio of x to y in the compound is

- (a) 1 : 1 (b) 1 : 2 (c) 1 : 3 (d) 1 : 4

9. In the estimation of nitrogen by Duma's method, 1.18 g of an organic compound gave 224 mL of N_2 at NTP. The percentage of nitrogen in the compound is

- (a) 20.01 (b) 11.87 (c) 47.73 (d) 23.72

10. When 0.35 g of an organic compound is heated with HNO_3 and $AgNO_3$ in a Carius tube, it gives 0.70 g of silver chloride. The percentage of chlorine in the compound is

- (a) 54.8% (b) 49.47%
 (c) 34.6% (d) 25.85%

SECTION - II

More than One Options Correct Type

11. Which of the following statements about paper chromatography is/are incorrect?

- (a) Moving phase is liquid and stationary phase is solid.
 (b) Moving phase is liquid and stationary phase is liquid.
 (c) Moving phase is solid and stationary phase is solid.
 (d) Moving phase is solid and stationary phase is liquid.

12. Which of the following is /are not an electrophile?

- (a) Na^+ (b) Li^+ (c) H^+ (d) Ca^{2+}

13. Chromatographic technique is used in the separation of

- (a) sugars (b) amino acids
 (c) plant pigments (d) volatile liquids.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

In Lassaigne's test, the organic compound is fused with sodium metal when nitrogen, sulphur, and halogens are converted into their corresponding ionic compounds. If only nitrogen is present, blue or green colouration is produced and if both nitrogen and sulphur are present, sometimes a blood red colouration is produced in the Lassaigne's test. If only sulphur is present, violet colouration is produced when sodium nitroprusside solution is added to the Lassaigne's extract.

14. The red colour produced in the Lassaigne's extract is due to formation of
 (a) $[\text{Fe}(\text{CNS})_2]^+$ (b) $[\text{Fe}(\text{CNS})_2]^{2+}$
 (c) $\text{Fe}(\text{CN})_3$ (d) $\text{Fe}(\text{SCN})_3$
15. The violet colouration is due to the formation of
 (a) $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ (b) $[\text{Fe}(\text{NO})_5\text{CN}]^+$
 (c) $[\text{Fe}(\text{CN})_5\text{NOS}]^{4-}$ (d) $[\text{Fe}(\text{CN})_5\text{NOS}]^{3-}$

Paragraph for Questions 16 and 17

Hyperconjugation describes the orbital interaction between π -system and the adjacent σ bond of the substituent group in organic compounds. Thus the sufficient condition for the hyperconjugation are

- (i) the presence of at least one sp^2 -hybrid carbon as in alkenes, carbocation and alkyl free radical.
 (ii) the presence of α -carbon, with at least one hydrogen, with respect of sp^2 -carbon atom.

More the number of hydrogen atoms attached on the α -carbon(s) of the sp^2 -hybrid carbon, more will the hyperconjugation, also called resonating structures of the compound.

Number of resonating structures due to hyperconjugation = $n + 1$, where n is the number of α -hydrogen.

16. Hyperconjugation is possible in
 (a) $\overset{+}{\text{C}}\text{H}_3$ (b) $\text{C}_6\text{H}_5\text{CH}_3$
 (c) $\text{CH}_2=\text{CH}_2$ (d) $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$
17. Which of the following has highest number of hyperconjugative structure?
 (a) 2-Ethylbut-2-ene (b) But-2-ene
 (c) *tert*-Butyl cation (d) Hex-2-ene

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the code given below the lists :

List I	List II
P. $\text{CH}_3-\text{CH}=\text{CH}_2 \leftrightarrow \text{H}^+\text{CH}_2=\text{CH}-\text{CH}_2^-$	1. -I-effect
Q. $\text{CH}_2=\text{CH}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}\text{I} \leftrightarrow \overset{-}{\text{C}}\text{H}_2-\text{CH}=\overset{+}{\text{C}}\text{I}$	2. -R-effect
R. $\text{CH}_2=\text{CH}-\overset{+}{\text{N}}(\text{O}^-)=\text{O} \leftrightarrow \overset{+}{\text{C}}\text{H}_2-\text{CH}=\overset{+}{\text{N}}(\text{O}^-)=\text{O}$	3. +R-effect
S. $\overset{\delta+}{\text{C}}\text{H}_3 \rightarrow \overset{\delta-}{\text{C}}\text{N}$	4. Hyperconjugation effect

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

19. Match the List I with List II and select the correct answer using the code given below the lists :

List I	List II
P. Diethyl ether, methyl isopropyl ether	1. Tautomers
Q. Acetaldehyde, vinyl alcohol	2. Chain isomers
R. <i>sec</i> -Butyl alcohol and <i>tert</i> -butyl alcohol	3. Functional isomers
S. Methyl cyanide, methyl isonitrile	4. Metamers

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

SECTION - V

Assertion Reason Type

20. **Assertion :** Glycerol can be purified by distillation under reduced pressure.
Reason : Liquid organic compounds are purified by distillation.

21. Assertion : Hydroxylamine (NH₂OH) contains N, and hence gives Prussian blue colour in Lassaigne's test.

Reason : Hydroxylamine with Na metal forms CN⁻ ion.

22. Assertion : Lithium can be used in place of sodium in Lassaigne's test.

Reason : Li generally forms ionic compounds.

SECTION - VI

Integer Value Correct Type

23. Amongst the following, the total number of

compounds which can be purified by sublimation is Sodium chloride, naphthalene, camphor, anthracene, iodine, benzoic acid.

24. The total number of isomers (including stereoisomers) with the molecular formula C₃H₅Cl is

25. Amongst the following, the total number of compounds which is/are not alicyclic heterocyclic is

Ethylene oxide, pyrrolidine, oxetane, dioxane, tetrahydrofuran, pyrrole, tropolone.

SOLUTIONS

STRUCTURE OF ATOM

1. (b): Cathode rays are never electromagnetic waves.

2. (c): Energy values are additive. Thus,

$$E = E_1 + E_2$$

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$$

$$\frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\lambda = 300 \text{ nm}, \lambda_1 = 760 \text{ nm}$$

$$\therefore \lambda_2 = 495.6 \text{ nm} \approx 496 \text{ nm}$$

3. (d): In photoelectric effect, kinetic energy and hence velocity is directly proportional to frequency of the incident light and independent of the intensity of light.

4. (b): $h\nu = h\nu_0 + (KE)$

$$KE = h(\nu - \nu_0)$$

$$(KE)_1 = h(3.2 \times 10^{16} - \nu_0), (KE)_2 = h(2.0 \times 10^{16} - \nu_0)$$

$$\text{Given, } (KE)_1 = 2(KE)_2$$

$$h(3.2 \times 10^{16} - \nu_0) = 2h(2.0 \times 10^{16} - \nu_0)$$

$$\therefore \nu_0 = 8.0 \times 10^{15} \text{ Hz}$$

5. (d): Radius of nucleus = $1.25 \times 10^{-13} \times A^{1/3} \text{ cm}$
 $= 1.25 \times 10^{-13} \times 64^{1/3} \text{ cm}$
 $= 1.25 \times 10^{-13} \times 4 \text{ cm}$
 $= 5 \times 10^{-13} \text{ cm}$

$$\text{Radius of atom} = 1 \text{ \AA} = 10^{-8} \text{ cm}$$

Fraction of atomic volume that is occupied by the nucleus :

$$\text{Volume of nucleus / Volume of atom}$$

$$= \frac{(4/3)\pi(5 \times 10^{-13})^3}{(4/3)\pi(10^{-8})^3} = \frac{125 \times 10^{-39}}{10^{-24}}$$

$$= 125 \times 10^{-15} = 1.25 \times 10^{-13}$$

n	l	Notation	Orbital	Electrons
1	0	1s	1	2
	1	1p	3	6
2	0	2s	1	2
	1	2p	3	6
	2	2d	5	10
3	0	3s	1	2
	1	3p	3	6
	2	3d	3	6
	3	3f	7	14

6. (c):

By Aufbau rule, electron will be filled in increasing order of energy, i.e., (n + l) rule. Minimum the value of (n + l), smaller is the energy of orbital.

$$1s < 1p < 2s < 2p < 3s < 2d \dots$$

V(Z = 23) will have electronic configuration as

$$1s^2 1p^6 2s^2 2p^6 3s^2 2d^5$$

7. (c): Spin multiplicity = (2S + 1).

↑ represents +1/2 and ↓ represents -1/2 spin values.

For $\uparrow \downarrow \downarrow$

$$S = -1/2$$

$$\therefore \text{Spin multiplicity} = 2 \times \left(-\frac{1}{2}\right) + 1 = 0$$

8. (a): $\frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

For Lyman series $n_1 = 1$, λ is shortest if $n_2 = \infty$

For H-atom Z = 1

$$\frac{1}{x} = R_H \left[\frac{1}{(1)^2} - \frac{1}{(\infty)^2} \right] \therefore R_H = \frac{1}{x}$$

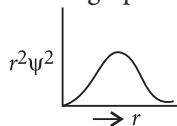
For Balmer series, $n_1 = 2$, λ is longest if $n_2 = 3$

For He, $Z = 2$

$$\frac{1}{\lambda_{\max}} = \left(\frac{1}{x} \right) (2)^2 \left[\frac{1}{2^2} - \frac{1}{3^2} \right]$$

$$\therefore \lambda_{\max} = \frac{9x}{5}$$

9. (c) : $l = 2$ represents d orbital for which radial distribution graph is represented as follows :



10. (a) : $E_n = -13.6 \left(\frac{Z^2}{n^2} \right) \text{ eV}$

$E_1(\text{H}) = -13.6 \text{ eV}$ in ground state, $n = 1$,

For H-atom, $Z = 1$

For Be, $Z = 4$

For first excited state, $n = 2$

$$E_2(\text{Be}^{3+}) = -\frac{13.6(4)^2}{(2)^2}$$

$$\therefore E_1 : E_2 = 1 : 4$$

11. (a,b,c) : Statement (a) is not correct because isotones have the same number of neutrons. Statement (b) is not correct as isobars differ in the number of neutrons because A is same but Z is different and neutrons = $A - Z$. Statement (c) is not correct because tritium (${}^3_1\text{H}$) is radioactive.

12. (b,c) : $l > n$ is not permissible; $m > l$ is not permissible.

13. (a, d) : The orbitals of same energy are called degenerate orbitals.

(a) (i) $3d_{xy}$ (ii) $3d_{yz}$

(b) (i) $3p_x$ (ii) $3d_{xy}$

(c) (i) $4s$ (ii) $3d_{xy}$

(d) (i) $3d_{x^2-y^2}$ (ii) $3d_{x^2-y^2}$

$3d_{xy}$ and $3d_{yz}$; $3d_{x^2-y^2}$ and $3d_{x^2-y^2}$ represent pair of degenerate orbitals.

14. (c)

15. (a) : Number of radial nodes = $n - l - 1$

Orbital	Radial nodes
4s	4 - 0 - 1 = 3
4p	4 - 1 - 1 = 2
3d	3 - 2 - 1 = 0
5f	5 - 3 - 1 = 1

16. (d) : Statement (d) is incorrect because all electromagnetic radiations travel with the velocity of light.

17. (c) : γ -rays : $10^{-16} - 10^{-11} \text{ m}$

Microwaves : $10^{-3} - 1 \text{ m}$

Radiowaves : $1 - 10^3 \text{ m}$

18. (b) : (P) Some α -particles deflected back shows presence of heavy body inside the atom.

(Q) Deflection of α -particles through small angle shows the presence of a positively charged body inside the atom.

(R) Passing of α -particles undeflected shows sufficient empty space in the atom.

(S) α -particle deflected back being very small shows that positively charged body occupies very small volume.

19. (c) : Wave number, $\bar{\nu} = \frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

For shortest wavelength ($\bar{\nu}_{\max}$) in Lyman series $n_1 = 1$, $n_2 = \infty$ and $Z = 1$ (for H-atom)

$$\text{Hence, } \frac{1}{\lambda} = \frac{1}{x} = R_H Z^2 \times \left[\frac{1}{1^2} - \frac{1}{\infty^2} \right] \Rightarrow R_H = \frac{1}{x}$$

(P) For shortest wavelength in Lyman series of Li^{2+} $n_1 = 1$, $n_2 = \infty$, $Z = 3$

$$\text{Hence, } \frac{1}{\lambda} = \frac{1}{x} \times 3^2 \times \left[\frac{1}{1^2} - \frac{1}{\infty^2} \right] = \frac{9}{x} \Rightarrow \lambda = \frac{x}{9}$$

(Q) For longest wavelength in Lyman series, $n_1 = 1$, $n_2 = 2$

$$\frac{1}{\lambda} = \frac{1}{x} \times 3^2 \times \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = \frac{27}{4x} \Rightarrow \lambda = \frac{4x}{27}$$

(R) For shortest wavelength in Balmer series, $n_1 = 2$, $n_2 = \infty$

$$\text{Hence, } \frac{1}{\lambda} = \frac{1}{x} \times 3^2 \times \left[\frac{1}{2^2} - \frac{1}{\infty^2} \right] \Rightarrow \lambda = \frac{4x}{9}$$

(S) For longest wavelength in Balmer series, $n_1 = 2$, $n_2 = 3$

$$\text{Hence, } \frac{1}{\lambda} = \frac{1}{x} \times 3^2 \times \left[\frac{1}{2^2} - \frac{1}{3^2} \right] \Rightarrow \lambda = \frac{4x}{5}$$

20. (c) : Electrons in different orbits have fixed energies.

21. (b)

$$22. (a) : \frac{1}{2}mv^2 = eV \text{ or } v = \sqrt{\frac{2eV}{m}}, \text{ i.e., } v \propto \sqrt{V}.$$

$$\lambda = \frac{h}{mv}, \text{ i.e. } \lambda \propto \frac{1}{v}$$

Hence, reason is correct explanation of assertion.

$$23. (3) : \text{Number of waves in an orbit} = \frac{\text{Circumference of orbit}}{\text{Wavelength}}$$

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

(Since angular momentums $mvr = nh/2\pi$)

For 3rd orbit, $n = 3$

$$24. (6) : \Delta x = 0.1 \text{ \AA} = 0.1 \times 10^{-10} \text{ m} = 10^{-11} \text{ m},$$

$$\Delta x(m\Delta v) = \frac{h}{4\pi} \text{ or } \Delta v = \frac{h}{4\pi m\Delta x}$$

$$= \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 9.11 \times 10^{-31} \text{ kg} \times 10^{-11} \text{ m}}$$

$$= 5.79 \times 10^6 \text{ m s}^{-1}$$

25. (5) : Let the number of the electrons in the ion be x .

$$\therefore \text{Number of neutrons} = x + \frac{30.4}{100}x = 1.304x$$

(\because Number of neutrons are 30.4% more than the number of electrons).

In the neutral atom, number of electrons = $x + 3$

(\because The ion carries + 3 charge.)

So, number of protons = $x + 3$

We know that, mass number = $n + p$

$$= 1.304x + x + 3 = 56$$

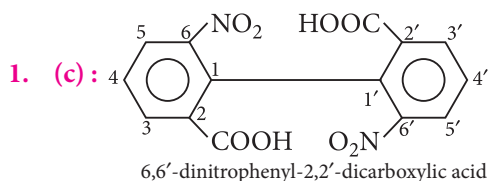
$$2.304x = 53, x = \frac{53}{2.304} = 23.003 \approx 23$$

$$\therefore \text{Number of electrons} = 23 + 3 = 26 = 5 \times 5 + 1$$

Comparing with $(5a + 1)$,

$$a = 5$$

ORGANIC CHEMISTRY : SOME BASIC PRINCIPLES AND TECHNIQUES



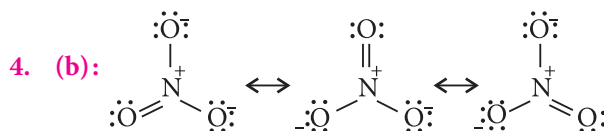
2. (b) : C_4H_4O represents furan. Therefore, it is heterocyclic and aromatic.

3. (a) : In case of same nucleophilic site, nucleophilicity parallel the basicity while in case of different sites, nucleophilicity varies inversely with electronegativity.

Order of electronegativity, $N > C$.

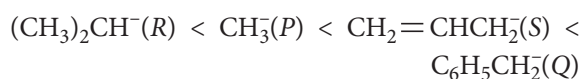
Thus, the order of nucleophilicity $C < N$

Among, $CH_3CH_2^-$, $HC\equiv C^-$ and $H_2C=CH^-$, $CH_3CH_2^-$ is the strongest nucleophile, as it is less electronegative (due to least s -character).



Since the three resonating structures are equivalent, each should make an equal contribution to the overall hybrid. The three N—O bonds should therefore be of equal length, and each oxygen atom should bear equal ($-2/3$) charge.

5. (b) : Both $CH_2=CHCH_2^-$ and $C_6H_5CH_2^-$ are stabilised by resonance but delocalisation of π -electrons over the benzene ring makes $C_6H_5CH_2^-(Q)$ more stable than $CH_2=CHCH_2^-(S)$. Further, +I-effect of the alkyl groups decreases the stability of carbanions. Therefore, $(CH_3)_2CH^-(R)$ is less stable than $CH_3^-(P)$ group. Thus, the overall stability increases in the order :



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Q1. What is the distance between K shell and L shell and M shell or likewise of an atom? Is it fixed for all the elements?

(Nivedita Pal)

Ans. For hydrogen like species, the radii of stationary states, r_n are given by the formula :

$$r_n = \frac{a_0 n^2}{Z}$$

where, $a_0 = 52.9$ pm, radius of the first stationary state

$n = 1, 2, 3, \dots$ (energy levels)

$Z =$ Atomic number

For K, L, M and N shell, the value of n is 1, 2, 3 and 4 respectively.

Now, considering H-atom first,

$$r_{K \text{ shell}} = a_0 \frac{(1)^2}{1} = a_0 \quad (\because Z = 1 \text{ for H})$$

$$r_{L \text{ shell}} = a_0 \frac{(2)^2}{1} = 4a_0; \quad r_{M \text{ shell}} = a_0 \frac{(3)^2}{1} = 9a_0$$

Now, distance between K shell and L shell

$$= r_{L \text{ shell}} - r_{K \text{ shell}} \\ = 4a_0 - a_0 = 3a_0$$

Distance between L shell and M shell = $r_{M \text{ shell}} - r_{L \text{ shell}}$

$$= 9a_0 - 4a_0 = 5a_0$$

Thus, $r_{L \text{ shell}} - r_{K \text{ shell}} \neq r_{M \text{ shell}} - r_{L \text{ shell}}$

Now, considering Li^{2+} ion,

For Li, $Z = 3$

$$r_{K \text{ shell}} = a_0 \frac{(1)^2}{3} = \frac{a_0}{3} = 0.33a_0$$

$$r_{L \text{ shell}} = \frac{a_0 (2)^2}{3} = \frac{4}{3}a_0 = 1.33a_0$$

$$r_{M \text{ shell}} = \frac{a_0 (3)^2}{3} = 3a_0$$

Distance between K shell and L shell = $r_{L \text{ shell}} - r_{K \text{ shell}}$

$$= 1.33a_0 - 0.33a_0 = a_0$$

Distance between L shell and M shell = $r_{M \text{ shell}} - r_{L \text{ shell}}$

$$= 3a_0 - 1.33a_0 = 1.67a_0$$

Thus, $r_{L \text{ shell}} - r_{K \text{ shell}} \neq r_{M \text{ shell}} - r_{L \text{ shell}}$

Also, $(r_{L \text{ shell}} - r_{K \text{ shell}})_{\text{H}} \neq (r_{L \text{ shell}} - r_{K \text{ shell}})_{\text{Li}^{2+}}$

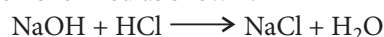
$(r_{M \text{ shell}} - r_{L \text{ shell}})_{\text{H}} \neq (r_{M \text{ shell}} - r_{L \text{ shell}})_{\text{Li}^{2+}}$

With increase in atomic number, the distance between the shells decreases.

Q2. What will be the graph between conductance and pH of the solution when titration is done taking NaOH in beaker and HCl in burette? Also, what will be the graph between pH of the solution w.r.t. volume of HCl added? Please explain.

(Soumya Tripathy)

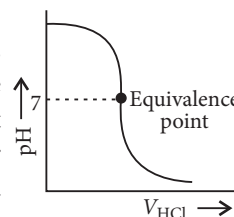
Ans. NaOH being a strong base, is completely ionised in solution. The conductivity of the solution is high due to highly mobile OH^- ions. Now, when HCl, a strong acid is added to NaOH solution, neutralisation reaction occurs and unionised water is formed as shown :



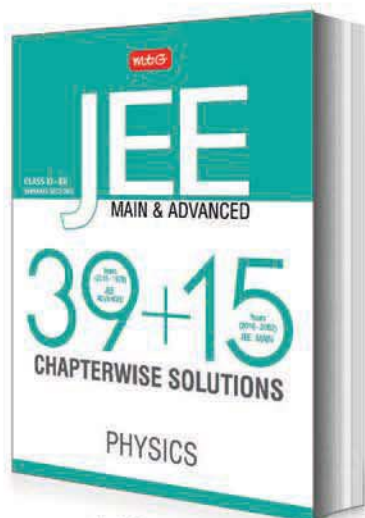
Here, highly mobile OH^- ions are replaced by less mobile Cl^- ions, and thus, conductivity of the solution decreases. Due to neutralisation of NaOH by HCl, the pH of the solution decreases. This happens till the equivalence point is reached. At the equivalence point, NaOH solution is completely neutralised by HCl solution and the solution is neutral in nature. After the equivalence point, when HCl is further added the conductivity increases sharply due to highly conducting H^+ ions and pH also decreases due to high concentration of H^+ ions.

Graph between pH of solution vs V_{HCl} is as follows:

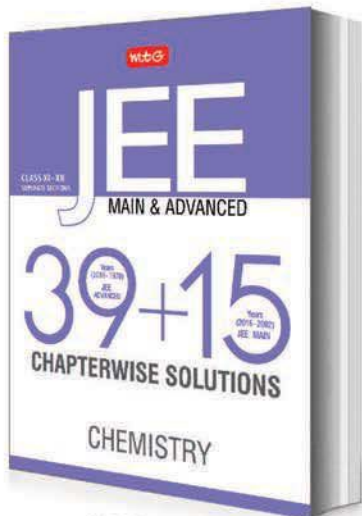
Initially, when HCl is added the pH of solution decreases slowly but near the equivalence point, abrupt change of pH occurs. After that solution is acidic and on further addition of HCl, pH decreases slowly.



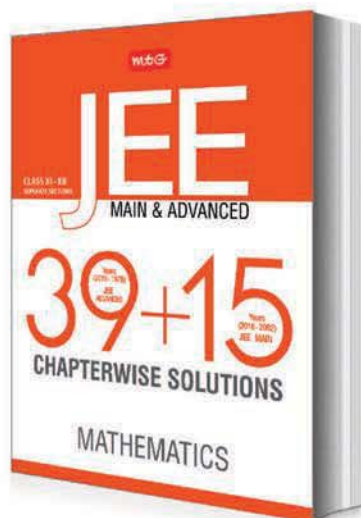
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CLASS XI Series 2

ACE YOUR WAY CBSE



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

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

- All questions are compulsory.
- Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- Q. no. 23 is a value based question and carries 4 marks.
- Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- Use log tables if necessary, use of calculators is not allowed.

- Is it correct to say that bond order always increases when an electron is lost?
 - In terms of electronic configuration, what do the elements of a given period and a group have in common?
 - Explain why chlorine can be converted into chloride ion more easily as compared to fluoride ion from fluorine.
 - The first ionisation enthalpy of chlorine atom is 1250 kJ/mol. State which of the following value would be more likely the ionisation enthalpy for the iodine atom? Explain.
 - 1000 kJ/mol
 - 1400 kJ/mol
 - How does bonding molecular orbital in a molecule of hydrogen differ from its antibonding molecular orbital?
 - The S—O bond lengths in SO_2 molecule are identical. Explain.
 - Arrange the elements N, P, O and S in the order of
 - increasing first ionisation enthalpy.
 - increasing non-metallic character.Give reason for the arrangement assigned.
 - Which element has the most positive electron gain enthalpy, and why?
Fluorine, nitrogen and neon.
 - Which of the following species have similar shape and why?
 NO_2^- , NO_2^+ , CO_2 , O_3
- OR**
- Use molecular orbital theory to explain why does the Be_2 molecule not exist.
- Would you expect the second electron gain enthalpy of oxygen as positive, more negative or less negative than the first? Justify your answer.
 - What are the conditions for the combination of atomic orbitals?

12. The first ($\Delta_i H_1$) and the second ($\Delta_i H_2$) ionisation enthalpies (kJ mol^{-1}) of three elements I, II and III are given below :

	I	II	III
$\Delta_i H_1$	403	549	1142
$\Delta_i H_2$	2640	1060	2080

Identify the element which is likely to be

- (i) a non-metal
 (ii) an alkali metal
 (iii) an alkaline earth metal
13. Write the favourable factors for the formation of ionic bond.
14. (i) What is the basis of classifying the elements in the modern periodic table?
 (ii) Lanthanoids and actinoids are placed in separate rows at the bottom of the periodic table. Explain the reason for this arrangement.
 (iii) Which family of elements has the electronic configuration $ns^2 np^2$?
15. 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^+ .

OR

- (i) PF_5 is known, whereas NF_5 is not. Explain.
 (ii) F_2 is a gas while I_2 is a solid. Explain.
 (iii) Out of H and H_2 , H has higher first ionisation energy while out of O and O_2 , O_2 has higher first ionisation energy. Explain why?
16. (i) Calculate the electronegativity of carbon if $E_{\text{H-H}} = 104.2 \text{ kcal mol}^{-1}$, $E_{\text{C-C}} = 83.1 \text{ kcal mol}^{-1}$, $E_{\text{C-H}} = 98.8 \text{ kcal mol}^{-1}$, $\chi_{\text{H}} = 2.1$
 (ii) Which element in periodic table has highest ionisation energy (IE)?
 (iii) Which element is more metallic Mg or Al and why?
17. (i) Which of the two, peroxide ion or superoxide ion, has a larger bond length?
 (ii) Which d -orbital is involved in sp^3d hybridisation and why?
18. (i) Energy of an electron in the ground state of the hydrogen atom is $-2.18 \times 10^{-18} \text{ J}$. Calculate the ionisation enthalpy of atomic hydrogen in terms of J mol^{-1} .

- (ii) Explain why cations are smaller and anions larger in radii than their parent atoms?
19. (i) Why are the lone pair-lone pair repulsions stronger than the lone pair-bond pair repulsions?
 (ii) ClF_3 is a T-shaped molecule while NF_3 has a trigonal pyramidal shape. Explain.
20. Among the elements of the second period Li to Ne pick out the element :
- (i) with the highest electronegativity
 (ii) that is the most reactive non-metal
 (iii) that is the most reactive metal.
21. (i) How bond energy varies from N_2^- to N_2^+ and why?
 (ii) On the basis of molecular orbital theory what are the similarities between
 (a) F_2 , O_2^{2-} (b) CO , N_2 , NO^+ ?
22. (i) Out of p -orbital and sp -hybrid orbital which has greater directional character and why?
 (ii) BH_4^- and NH_4^+ are isostructural. Explain.
 (iii) Why axial bonds of PCl_5 are longer than equatorial bonds?

23. Ashish always tried to understand the theoretical concepts learnt in his class better by performing the experiment in laboratory, whenever possible. Once, he studied about solubility of different compounds in water. Then under the supervision of his teacher he took potassium chloride, calcium carbonate, ethanol and ethyl amine and try to dissolve in water one by one. He was surprised that all the four compounds are dissolved in water and discussed this result with his teacher.
- (i) Why did Ashish think that only certain compounds are soluble in water but others are not?
 (ii) What explanation was given by the teacher? Explain.
 (iii) What values are associated with Ashish?
24. Define hydrogen bond. Also explain the conditions required for H-bonding and the types of it with example. Is it weaker or stronger than the van der Waals forces?

OR

- (i) Explain the following :
- (a) Whether ClO_2^- ion is linear or not?
 (b) Whether the geometry of XeF_2 is linear or non-linear?

(c) Whether PCl_3 molecule is polar or non-polar?

(ii) BF_3 and graphite both are coplanar having sp^2 hybridisation but later is a good conductor. Explain.

25. (i) Explain why :

(a) The covalent radius of an atom is smaller than the metallic radius of the atom.

(b) Why H_2O is a liquid while H_2S is a gas?

(ii) (a) Explain why the substantial decrease in first ionisation enthalpy is observed between Na and K, and Mg and Ca, is not observed between Al and Ga.

(b) What is the significance of the large increase in the third ionisation enthalpy of Ca and the fifth ionisation enthalpy of Si?

(c) Which would you expect to be larger, the first ionisation enthalpy of Rb or Sr and Cl or Br? Explain why.

OR

(i) Illustrate by taking examples of transition elements and non-transition elements that oxidation states of elements are largely based on electronic configuration.

(ii) All transition elements are d -block elements, but all d -block elements are not transition elements. Explain.

(iii) By what name are the elements belonging to the f -block called?

26. (i) Discuss the shapes of the following molecules on the basis of valence bond theory : BeF_2 and CH_4 .

(ii) Explain how valence bond theory differs from the Lewis concept.

(iii) Which out of the two molecules OCS and CS_2 has a higher dipole moment and why?

OR

(i) Why is the concept of resonance needed? What is a resonance hybrid? How does it differ from the resonance structures drawn for a molecule?

(ii) Account for the following :

(a) Noble gases are chemically unreactive.

(b) Low ionization enthalpy and high electron gain enthalpy favour ionic bond formation.

(iii) Write the significance of a plus and a minus sign shown in representing the orbitals.

SOLUTIONS

1. Bond order may increase or decrease when an electron is lost depending upon whether the electron is lost from antibonding or bonding molecular orbital respectively.

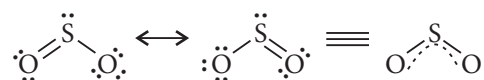
2. Elements of a particular period have same number of electronic shells and for elements in a particular group, the number of electrons in the outermost shell is same.

3. Electron gain enthalpy of Cl is more negative than that of F. This is due to small size of fluorine and hence the valence electrons of fluorine causes more repulsion to the incoming electron.

4. The more likely value of IE for iodine atom would be 1000 kJ/mol because ionisation enthalpy tends to decrease with atomic number in a group.

5. Bonding MO of hydrogen has lower energy than antibonding MO and has two electrons whereas in antibonding MO of hydrogen has higher energy and is empty.

6. The S—O bond lengths in SO_2 molecule are the same because of resonance in SO_2 . The sulphur dioxide molecule is resonance hybrid of the following two structures.



7. (i) $S < P < O < N$

Ionisation enthalpy increases from left to right in a period and decreases down the group. N has higher ionisation enthalpy than O due to extra stability of half-filled orbitals. Similarly, P has higher ionisation enthalpy than S due to half-filled orbitals.

(ii) $P < S < N < O$

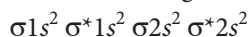
Non-metallic character decreases down the group and increases from left to right in a period.

8. Both nitrogen and neon have positive electron gain enthalpies but neon has a much greater positive electron gain enthalpy because of its much more stable close shell electronic configuration than the less stable exactly half-filled electronic configuration of nitrogen.

9. NO_2^+ and CO_2 are sp hybridised, therefore, they have linear shape. NO_2^- and O_3 are sp^2 hybridised. Therefore, their shape is angular or V-shaped.

OR

There should be 8 electrons in Be_2 molecule. The MO electronic configuration must be



$$N_b = 4 \text{ and } N_a = 4$$

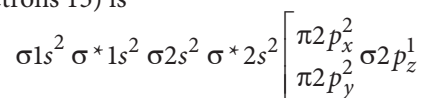
$$\text{Bond order of } \text{Be}_2 \text{ is } \frac{1}{2}(4 - 4) = 0$$

Be_2 molecule is therefore unstable and does not exist.

10. When an electron is added to oxygen atom to form ion, energy is released. Hence, first electron gain enthalpy of oxygen is negative. But when another electron is added to O^- ion to form O^{2-} ion, it feels stronger electrostatic repulsion. Hence, addition of second electron takes place with absorption of energy. That's why the second electron gain enthalpy of oxygen is positive.
11. The conditions for the combination of atomic orbitals are :
- The combining atomic orbitals must have the same or nearly the same energy.
 - The combining atomic orbitals must have the same symmetry about the molecular axis.
 - The combining atomic orbitals must overlap to the maximum extent.
12. (i) Element III is a non-metal. Ionisation enthalpies of non-metals are very high.
(ii) An alkali metal has very low first ionisation enthalpy and much higher second ionisation enthalpy. Therefore, element I is an alkali metal.
(iii) An alkaline earth metal has higher first ionisation enthalpy ($\Delta_i H_1$) but lower $\Delta_i H_1 + \Delta_1 H_2$ than the alkali metal of the same period. Therefore, element II is an alkaline earth metal.
13. The following factors facilitate the formation of an ionic bond between a metal and a non-metal :
- Ionisation energy** : Lesser the ionisation energy, greater is the ease of formation of a cation.
 - Electron affinity** : High electron affinity favours formation of an anion.
 - Lattice Energy** : It is defined as the amount of energy released when cations and anions are brought close to each other from infinity to their respective equilibrium sites in the crystal

lattice to form one mole of the ionic compound. The higher the magnitude of the lattice energy, the greater is the tendency of the formation of an ionic bond.

14. (i) The basis of classifying the elements in the modern periodic table is that physical and chemical properties of the elements are a periodic function of their atomic numbers.
(ii) These have been placed separately at the bottom of the periodic table for convenience. If they are placed within the body of the periodic table, the periodic table will become extremely long and inappropriate.
(iii) The family of elements which has the electronic configuration $ns^2 np^2$ is carbon family, that is group 14.
15. (i) In He_2 total 4 electrons are present. Its MO electron 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 MO electronic configuration of N_2^+ (total electrons 13) is



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^+ ($\sigma 1s^1$) is $\frac{1}{2}$ and the bond order of He_2^+ ($\sigma 1s^2 \sigma^* 1s^1$) is also $\frac{1}{2}$.

As bond order is same, the bond dissociation energy of H_2^+ is almost same as that of He_2^+ .

OR

- (i) Phosphorus has vacant d -orbitals in its valence shell and therefore, can extend its bonding beyond octet. Nitrogen does not have d -orbitals in its valence shell and therefore, cannot expand its valence shell beyond four. As a result, N cannot form pentahalides such as NF_5 .
(ii) The strength of intermolecular forces (van der Waals' type) increases down the group. It is for this reason, that there is a gradual change from gaseous state to solid as we go down in the group.

(iii) In H_2 , first electron is removed from $\sigma(1s)$ which has lower energy than $1s$ -orbital of H-atom. However, in O_2 , first electron is removed either from $\pi^*(2p_y)$ or $\pi^*(2p_x)$ orbital which has higher energy than $2p$ -orbital of O-atom.

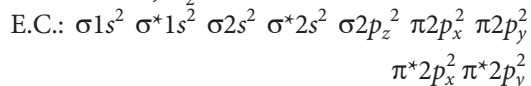
16. (i) We know that, $\chi_C - \chi_H = 0.208\sqrt{\Delta}$
 $\Delta = E_{C-H} - \sqrt{E_{C-C} \times E_{H-H}}$
 $= 98.8 - \sqrt{83.1 \times 104.2} = 98.8 - 93.05 = 5.75$
 $\therefore \chi_C - \chi_H = 0.208\sqrt{5.75} = 0.498$
 $\chi_C = 0.498 + \chi_H = 0.498 + 2.1$
 $= 2.59 \approx 2.6$

(ii) He has highest ionisation energy as it increases on moving from left to right and decreases down the group and He is placed at top right corner of periodic table.

(iii) Mg is more metallic due to lower ionisation energy.

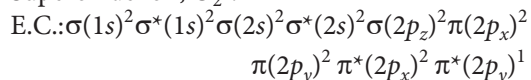
17. (i) The bond length in a molecule depends on bond order. The higher the bond order, smaller will be the bond length.

Peroxide ion, O_2^{2-} :



$$\text{Bond order} = \frac{10 - 8}{2} = 1$$

Superoxide ion, O_2^- :



$$\text{Bond order} = \frac{10 - 7}{2} = 1.5$$

Bond order of superoxide is higher than peroxide ion, hence bond length of peroxide ion is larger.

(ii) The d-orbital involved in sp^3d hybridisation is d_{z^2} . The three planar triangular hybrid orbitals may be assumed to be formed from one s - and two p -orbitals, i.e., sp^2 hybridisation and the remaining one p -orbital may combine with d_{z^2} to form two axial hybrid orbitals that results in the formation of sp^3d hybridised orbitals.

18. (i) Energy of the electron in the ground state of H-atom, $E_1 = -2.18 \times 10^{-18}$ J
 Ionisation energy = $E_\infty - E_n$
 Ionisation enthalpy per mole of atomic hydrogen = $(E_\infty - E_1) N_A$

$$= [0 - (-2.18 \times 10^{-18})] \times 6.023 \times 10^{23}$$

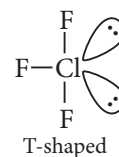
$$= 2.18 \times 6.023 \times 10^5 \text{ J/mol} = 13.13 \times 10^5 \text{ J/mol}$$

$$= 1.313 \times 10^6 \text{ J/mol}$$

(ii) A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same thus, the effective nuclear charge per electron increases. The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge.

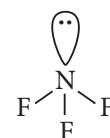
19. (i) Lone pairs are the electron pairs which do not participate in the bond formation. These are localised on the central atom and occupy more space as compared to the bond pairs. This causes greater repulsions between lone pairs of electrons as compared to the lone pair-bond pair and bond pair-bond pair repulsions.

(ii) In the case of ClF_3 molecule, there are three bond pairs and two lone pairs of electrons. As the lone pair-lone pair repulsion is more than lone pair-bond pair repulsion, which is more than bond pair-bond pair repulsion, the lone pairs occupy the equatorial positions as there are lesser repulsions at that position compared to the axial position in which there are more repulsions. Hence, it is T-shaped molecule.



T-shaped

In the case of NF_3 molecule, it has three bond pairs and one lone pair. The actual geometry of the molecule should be tetrahedral and due to lone pair-bond pair repulsions its shape is trigonal pyramidal.



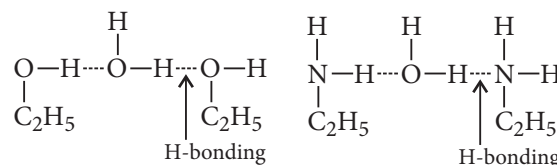
Trigonal pyramidal

20. (i) The electronegativity increases in going from left to right and decreases down the group. Therefore, the element with the highest electronegativity in second period is F.

- (ii) The reactivity of a non-metal can be estimated from its electronegativity. The non-metal having higher electronegativity should be more reactive. Thus, the most reactive non-metal is F.
- (iii) The reactivity of metals is estimated by the ionisation energy. The metal having lower ionisation energy should be more reactive. Thus, here Li is the most reactive metal.
21. (i) Bond energy of N_2^+ = Bond energy of N_2^- . This is because they have the same bond order value of 2.5. However, for N_2 bond order is 3 hence, it has higher bond energy than other two ions. Though considering the bond energies more precisely, N_2^- is slightly less stable and hence has less bond energy than N_2^+ due to presence of greater number of electrons in the antibonding molecular orbitals in N_2^- .
- (ii) (a) F_2 and O_2^{2-} have same bond order of 1 due to same molecular orbital electronic configuration. Hence, these are assumed to have same bond energy and bond length.
(b) Similarly CO , N_2 and NO^+ have same molecular orbital electronic configuration thus, they have same bond order and bond length.
22. (i) sp -orbital has greater directional character than p -orbital. This is because p -orbital has equal sized lobes with equal electron density in both the lobes whereas sp -hybrid orbital has greater electron density on one side.
- (ii) In BH_4^- , B contributes three valence electrons and one each by four H atoms and one negative charge sum up to give 4 valence shell electron pair to give sp^3 hybridisation and tetrahedral structure. In NH_4^+ , N contributes five valence electrons, four electrons by four H atoms minus one electron for positive charge to give four valence shell electron pairs thus, sp^3 hybridisation and tetrahedral shape.
- (iii) This is due to greater repulsion on the axial bond pairs by the equatorial bond pairs of electrons.
23. (i) Ashish thinks so because the former two compounds *i.e.*, potassium chloride and calcium carbonate are ionic in nature whereas the later two compounds *i.e.*, ethanol and ethyl

amine are covalent in nature which should be insoluble in water.

- (ii) Teacher told him that the former two compounds dissolved because of their ionic nature whereas the later two dissolved because of H-bonding with the water molecules.



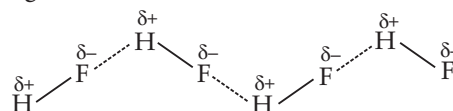
- (iii) Values shown by Ashish is experimental aptitude, curious, serious about his studies.

24. Hydrogen bond can be defined as an attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule. Following conditions should be fulfilled by a molecule for the formation of hydrogen bond.

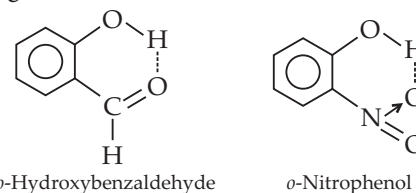
- (i) Hydrogen atom should be linked to a highly electronegative atom, such as F, O or N through a covalent bond.
- (ii) The size of the electronegative atom bonded covalently to the hydrogen atom should be small.

Types of H-bonding :

Intermolecular hydrogen bond : When hydrogen bond is formed between the hydrogen atom of one molecule and the electronegative atom of another molecule of the same compound (such as HF) or different compounds (such as water and alcohol), it is known as intermolecular hydrogen bond.



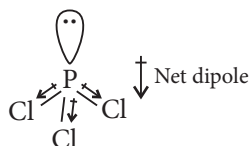
Intramolecular hydrogen bond : When hydrogen bond is formed between the hydrogen atom and an electronegative atom, present in the same molecule, it is known as intramolecular hydrogen bond.



H-bonding is stronger than van der Waals forces.

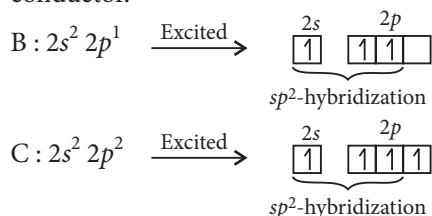
OR

- (i) (a) ClO_2^- ion has two bonding and two non-bonding electron pairs around chlorine, *i.e.*, chlorine atom undergoes sp^3 hybridisation. Tetrahedral configuration comes into existence. Two positions are occupied by oxygen atoms and other two positions are occupied by two lone pairs of electrons. Thus, the ion has V-shape *i.e.*, it is non linear.
- (b) In XeF_2 , two bonding and three non-bonding electron pairs are present, *i.e.*, xenon atom undergoes sp^3d hybridization. Trigonal bipyramid configuration comes into existence. Non-bonding electron pairs always occupy the equatorial positions and thus, fluorine atoms occupy the axial positions. Hence, F—Xe—F molecule is linear.
- (c) In PCl_3 , three bonding and one non-bonding electron pairs are present, *i.e.*, phosphorus atom undergoes sp^3 hybridization giving tetrahedral configuration. Three positions are occupied by chlorine atoms and one by lone pair.



The electronegativity of Cl is more than P. Thus, P—Cl bond is polar in nature. On account of structure, the molecule should be polar in nature as the bond poles add to give a net dipole moment.

- (ii) Both BF_3 and graphite have sp^2 hybridisation but in graphite one mobile electron is present on each carbon atom which makes it a good conductor.



25. (i) (a) In a metallic lattice the valence electrons are mobile, therefore, they are only weakly attracted by the metal ions or kernels. In contrast in a covalent bond, a pair of electrons is strongly attracted by the nuclei of two atoms.

Thus, a metallic radius is always more than its covalent radius.

- (b) In H_2O , there is hydrogen bonding and hence H_2O molecules are associated but in H_2S there is no hydrogen bonding.
- (ii) (a) In Na (186 pm) and K (231 pm), and Mg (160 pm) and Ca (180 pm) there is adequate increase in atomic size which is not observed in case of Al (118 pm) and Ga (135 pm). As size of the atom increases, ionisation energy decreases thus, there is no substantial decrease in ionisation enthalpy in case of Al and Ga.
- (b) Ca after losing 2 electrons and Si after losing 4 electrons acquire the nearest noble gas configuration, which means both of them acquire a stable completely filled configuration. Thus, large amount of energy is required to remove third electron from Ca and fifth electron from Si.

(c) Out of Rb and Sr, Sr will have greater first ionisation enthalpy because of its small size. As we move from left to right in the periodic table, the atomic size decreases due to increase in effective nuclear charge and more energy is required to remove electron from the outermost shell.

Out of Cl and Br, Cl will have greater ionisation enthalpy because of its small atomic size. As we move down a group in the periodic table the atomic size increases due to addition of an extra valence shell so, it is easier to remove an electron from the outermost shell.

OR

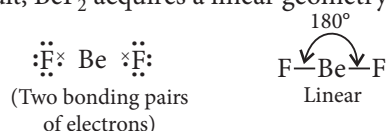
- (i) The oxidation state of an element is based on its electronic configuration. The various oxidation states of a transition metal is due to the involvement of $(n-1)d$ and outer ns electrons in bonding. For example, $\text{Ti}(22) : [\text{Ar}] 3d^2 4s^2$ can show three oxidation states (+2, +3 and +4) in various compounds like $\text{TiO}_2(+4)$, $\text{Ti}_2\text{O}_3(+3)$ and $\text{TiO}(+2)$.

The non-transition elements mainly the p -block elements can show a number of oxidation states from $+n$ to $(n-8)$ where, n is the number of electrons present in the outermost shell *e.g.*, phosphorus can show -3 , $+3$ and $+5$ oxidation states.

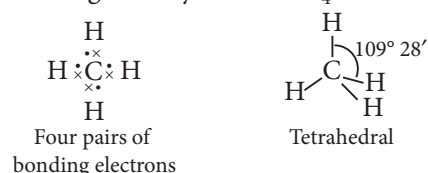
Lower oxidation states are ionic as the atom accepts the electron or electrons to achieve stable configuration while higher oxidation states are achieved by unpairing the paired electrons and shifting the electrons to vacant *d*-orbital.

- (ii) According to the definition of transition metals the elements should have incomplete penultimate ($n - 1$) shell. But few *d*-block elements have completely filled penultimate shell, they are not considered as transition metals. *e.g.*, $\text{Zn}(3d^{10}4s^2)$, $\text{Cd}(4d^{10}5s^2)$ and $\text{Hg}(5d^{10}6s^2)$.
- (iii) The *f*-block elements in which *4f* orbitals are progressively filled are called lanthanides, whereas those in which *5f* orbitals are progressively filled are called actinides.

26. (i) BeF_2 : Be atom has two electrons in its outermost shell. Each fluorine atom is short of its octet by one electron. Thus, there are two bonding pairs of electrons around Be. As a result, BeF_2 acquires a linear geometry.



CH_4 : Carbon atom has four electrons in its valence shell. Each hydrogen atom has one electron each. Thus, there are four bonding pairs of electrons around the carbon atom. These four pairs of bonding electrons gives tetrahedral geometry for the CH_4 molecule.



- (ii) The Lewis concept describes the formation of bond in terms of sharing one or more electron pairs and the octet rule. It does not explain the energetics of the bond formation, and shapes of the polyatomic molecules. The valence bond theory describes the bond formation in terms of hybridisation and overlap of the orbitals. The overlap of orbitals along the internuclear axis increases the electron-density between the two nuclei resulting in a decrease in the energy and formation of a bond.

(iii)

OCS (Carbonyl sulphide)	CS ₂ (Carbon disulphide)
$\text{O}=\text{C}=\text{S}$ $\leftarrow + \quad + \rightarrow$ (Linear molecule)	$\text{S}=\text{C}=\text{S}$ $\leftarrow + \quad + \rightarrow$ (Linear molecule)
C=O bond is more polar and C=S bond has very little polarity. Net dipole: Non-zero ($\leftarrow +$)	C=S bond has a very small dipole and the two dipoles cancel each other Net dipole: Zero

OR

- (i) Lewis structures are often inadequate, without the concept of resonance, to describe the distribution of electrons in certain molecules and ions. Sometimes, more than one Lewis structure is needed to describe a molecule. These structures differ only in the placement of electrons. Resonance describes more fully the distribution of electrons in a molecule.

A resonance hybrid is the true structure of a molecule or polyatomic ion, whereas the various resonance structures that are used to depict the hybrid do not individually have any reality. The hybrid is a mix, or average, of the various resonance structures that compose it.

- (ii) (a) The outermost configuration of noble gas is completely filled and is very stable, for example Ne, Xe, Ar, etc. have no tendency to gain, lose electrons or even share their electrons.
- (b) The low ionization enthalpy allows the electron to be removed easily, that is, formation of a positive ion and hence greater the chances of formation of an ionic bond. High electron gain enthalpy implies a large amount of energy is released (exothermic process) when an electron is added to an isolated gaseous atom, and thus more stable will be the negative ion produced. Consequently, the probability of formation of ionic bond is enhanced.
- (iii) As orbitals are represented by wave functions, a plus sign in an orbital represents a positive wave function and a minus sign represents a negative wave function.



MPP-2 MONTHLY Practice Problems

Class XI



This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Structure of Atom | Classification of Elements and Periodicity in Properties

Total Marks : 120

Time Taken : 60 Min.

NEET / AIIMS

Only One Option Correct Type

- Visible spectrum of hydrogen shows that it exists in two different forms which are based on direction of spin of the
 - molecule of hydrogen
 - nuclei of hydrogen atoms
 - electrons of hydrogen
 - atoms of hydrogen molecule.
- The statement that is not true for the long form of the periodic table is
 - it reflects the sequence of filling the electrons in the order of sub-energy levels *s*, *p*, *d* and *f*.
 - it helps to predict the stable valency states of the elements
 - it reflects trends in physical and chemical properties of the elements
 - it helps to predict the relative ionicity of the bond between any two elements.
- With what velocity must an electron travel so that its momentum is equal to that of a photon of wavelength 5200 Å?
 - 756 m s^{-1}
 - 1938 m s^{-1}
 - 1420 m s^{-1}
 - 1398 m s^{-1}
- An element *X* occurs in short period having configuration ns^2np^1 . The formula and nature of its oxide is
 - XO_3 , basic
 - XO_3 , acidic
 - X_2O_3 , amphoteric
 - X_2O_3 , acidic.
- If an electron, hydrogen, helium and neon nuclei are all moving with the velocity of light, then the wavelengths associated with these particles are in the order
 - electron > hydrogen > helium > neon
 - electron > helium > hydrogen > neon
 - electron > hydrogen > neon > helium
 - hydrogen > neon > helium > electron.
- The ionization enthalpies of Li and sodium are 520 kJ mol^{-1} and 495 kJ mol^{-1} respectively. The energies required to convert all the atoms present in 7 mg of Li vapours and 23 mg of sodium vapours to their respective gaseous cations are respectively
 - 52 J, 49.5 J
 - 520 J, 495 J
 - 49.5 J, 52 J
 - 495 J, 520 J
- In the discharge tube, the emission of cathode rays requires
 - low potential and low pressure
 - low potential and high pressure
 - high potential and high pressure
 - high potential and low pressure.
- Among the following, highest density is of
 - Ir
 - Os
 - Pb
 - Hg.
- Which of the following rules/principles is responsible to rule out the existence of definite paths or trajectories of electrons?
 - Aufbau rule
 - Hund's rule of maximum multiplicity
 - Pauli's exclusion principle
 - Heisenberg's uncertainty principle.
- The correct statement about *d*-block elements is
 - they are all metals
 - they show variable valency
 - they form coloured ions and complex salts
 - all the above statements are correct.

11. The nucleus of an atom can be assumed to be spherical. The radius of the nucleus of mass number A is given by $1.25 \times 10^{-13} \times A^{1/3}$ cm. Radius of atom is one Å. If the mass number is 64, then the fraction of the atomic volume that is occupied by the nucleus is

- (a) 1.0×10^{-3} (b) 5.0×10^{-5}
(c) 2.5×10^{-2} (d) 1.25×10^{-13}

12. CO_2 has the same geometry as

- (I) HgCl_2 (II) NO_2
(III) SnCl_4 (IV) C_2H_2
(a) I and III (b) II and IV
(c) I and IV (d) III and IV

Assertion & Reason Type

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

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. **Assertion :** Electrons behave like X-rays and display wave properties.

Reason : X-ray diffraction pattern and the electron diffraction pattern of aluminium foil are similar.

14. **Assertion :** Alkaline earth metal carbonates (BeCO_3) are soluble in water.

Reason : All ionic compounds are fairly soluble in water.

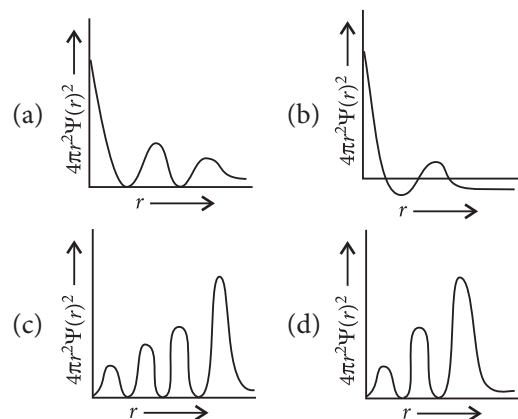
15. **Assertion :** The quantized energy of an electron is largely determined by its principal quantum number.

Reason : The principal quantum number, n is a measure of the most probable distance of finding the electron around the nucleus.

JEE MAIN / JEE ADVANCED / PETS

Only One Option Correct Type

16. Which of the following graphs between radial probability distribution and radius of atom corresponds to orbital with Azimuthal quantum number (l) equal to 0 and principal quantum number (n) equal to 4?



17. Which of the following pairs are chemically dissimilar?

- (a) Na and K (b) Ba and Sr
(c) Zr and Hf (d) Ca and Zn

18. α -particle of 6 MeV energy is scattered back from a silver foil. Calculate the maximum volume in which the entire positive charge of the atom is supposed to be concentrated. (Z for silver = 47)

$$K = 9.0 \times 10^9 \text{ Nm}^2\text{C}^{-2}.$$

- (a) $1.4 \times 10^{-40} \text{ m}^3$ (b) $4.8 \times 10^{-42} \text{ m}^3$
(c) $4.8 \times 10^{-41} \text{ m}^3$ (d) $6.2 \times 10^{-40} \text{ m}^3$

19. The correct order of covalent, van der Waals' and crystal radii is

- (a) $r_{\text{covalent}} < r_{\text{crystal}} < r_{\text{van der Waal}}$
(b) $r_{\text{covalent}} < r_{\text{van der Waal}} < r_{\text{crystal}}$
(c) $r_{\text{crystal}} < r_{\text{covalent}} < r_{\text{van der Waal}}$
(d) $r_{\text{crystal}} < r_{\text{van der Waal}} < r_{\text{covalent}}$

More than One Options Correct Type

20. The nucleus of an atom is located at $x = y = z = 0$ and the probability of finding an s -orbital electron in a tiny volume around $x = a, y = z = 0$ is 1.0×10^{-5} . Choose the correct statement(s) regarding the probability of electrons.

- (a) The probability of finding the electron in the same sized volume around $x = z = 0, y = a$ is the same *i.e.*, 1×10^{-5} .
(b) The probability of finding the electron in the same sized volume around $x = y = 0, z = a$ is zero.
(c) The probability at the second site if the electron were in a p_z -orbital is zero.
(d) The probability at the second site if the electron were in a p_z -orbital is the same *i.e.*, 1.0×10^{-5} .

21. Which of the following statements is incorrect with respect to the property of elements with an increase in atomic number in the carbon family (group 14)?
- Atomic size decreases
 - Ionisation energy increases
 - Metallic character decreases
 - Stability of +2 oxidation state increases
22. The radial distribution function $[P(r)]$ is used to determine the most probable radius, which is used to find the electron in a given orbital. If $\frac{dP(r)}{dr}$ for 1s-orbital of hydrogen like atom having atomic number Z , is $\frac{dP}{dr} = \frac{4Z^3}{a_0^3} \left(2r - \frac{2Zr^2}{a_0} \right) e^{-2Zr/a_0}$. Then which of the following statements is/are correct?
- At the point of maximum value of radial distribution function $\frac{dP(r)}{dr} = 0$; one antinode is present.
 - Most probable radius of Li^{2+} is $\frac{a_0}{3}$ pm.
 - Most probable radius of He^+ is $\frac{a_0}{2}$ pm.
 - Most probable radius of hydrogen atom is a_0 pm.
23. Which of the following statements is/are correct?
- The magnitude of the second electron affinity of sulphur is greater than that of oxygen.
 - The magnitude of the second electron affinity of sulphur is equal to that of oxygen.
 - The first electron affinities of bromine and iodine are approximately the same.
 - The first electron affinity of fluorine is greater than that of chlorine.

Integer Answer Type

24. If the lowest energy X-rays have $\lambda = 3.0 \times 10^{-8}$ m, estimating the minimum difference in energy between two Bohr orbits, where an electronic transition would correspond to the emission of an X-ray, at what minimum Z (atomic number) would a transition from the second energy level to the first result in the emission of an X-ray?
25. The value of n (i.e. principal quantum number) for the valence shell of palladium is (atomic number = 46)
26. Alveoli are tiny sacs in the lungs whose average diameter is 5×10^{-10} m. Consider an oxygen molecule (5.3×10^{-26} kg) trapped within a sac. Uncertainty in the velocity of oxygen molecules in m/s is

Comprehension Type

Quantum numbers are assigned to get complete information of electrons regarding their energy, angular momentum, spectral lines etc. Four quantum numbers are known :

Principal quantum number tells about the distance of electron from nucleus, energy of electron in a particular shell and its angular momentum. Azimuthal quantum number tells about the subshells in a given shell and of course shape of orbital. Magnetic quantum number deals with the study of orientations of degeneracy of a subshell. Spin quantum number which defines the spin of electron designated as $+\frac{1}{2}$ or $-\frac{1}{2}$ represented by \uparrow and \downarrow respectively. Electrons are filled in orbitals following Aufbau rule, Pauli's exclusion principle and Hund's rule of maximum multiplicity. On the basis of this, answer the following questions :

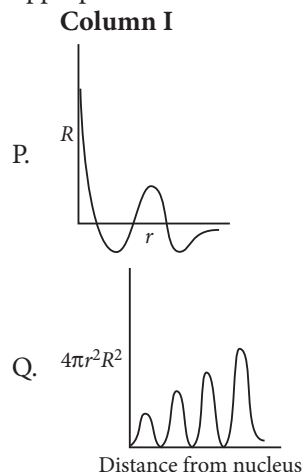
27. Number of electrons having the quantum numbers $n = 4, l = 0, s = -1/2$ in Zn^{2+} ion is/are
- 1
 - 0
 - 2
 - 5
28. Spin angular momentum for unpaired electron in sodium (Atomic No. = 11) is
- $\frac{\sqrt{3}}{2}$
 - $0.866 h/2\pi$
 - $-\frac{\sqrt{3}}{2} \frac{h}{2\pi}$
 - none of these

Matrix Match Type

29. Match the entries listed in Column I with appropriate entries listed in Column II.

Column I				Column II			
P.	$\text{Al}(\text{OH})_3$			1.	Weakly acidic		
Q.	$\text{TlOH}_{(aq)}$			2.	Weakly basic		
R.	H_2CO_3			3.	Neutral		
S.	$\text{NaNO}_{3(aq)}$			4.	Strongly basic		
	P	Q	R	S			
(a)	1	2	3	4			
(b)	4	1	2	3			
(c)	2	4	1	3			
(d)	3	2	4	1			

30. Match the entries listed in Column I with appropriate entries listed in Column II.



Column II

1. $4s$

2. $5p_y$

- R. Angular probability is dependent on θ and ϕ
- S. At least one angular node is present

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



Keys are published in this issue. Search now! ☺

SELF CHECK

No. of questions attempted
 No. of questions correct
 Marks scored in percentage

Check your score! If your score is

> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

Top-Ranked IIT Madras is Fifth Choice for JEE Toppers This Year

Institute has 103 takers, the same number as the previous year, though MHRD places it at no. 1

Flying in the face of a ministry of human resources development (MHRD) ranking of national engineering colleges that placed IIT Madras at the top, more than 60% of the top 1,000 rankers of JEE Advanced 2016 have chosen IIT Bombay, Delhi, Kanpur and Kharagpur. IIT Madras ranks at number 5 for the top rankers in the JEE Advanced with only 103 takers.

Last year too, 103 students opted for IIT Madras among the top 1,000 rankers. The MHRD under its National Institutional Ranking Framework (NIRF) first carried out the ranking in four categories — engineering, management, pharmacy and university — this April. More than 3,500 institutes had participated in this

edition, the process for which started in December 2015. The objective of the ranking is to facilitate choice and enable higher education stakeholders to make informed decisions.

However, the National Ranking Framework ranking has had no impact on the choice of institute among the top 1000 rankers. Around 262 of these

Of top 100, 67 opted for IIT Bombay and five for IIT Madras, says Joint Seat Allocation Authority. 196 have chosen IIT Delhi (compared to 194 last year), 167 of these selected IIT Kanpur (172 last year) and 106 chose IIT Kharagpur (107 last year).

With IIT Madras at the top, the other category A engineering institutes in the National Ranking are IIT Bombay, IIT Kharagpur, IIT Delhi, IIT Kanpur. "IIT B has been the number one choice for top rankers and this has been the trend since last eight years," said Ashok Misra, former director of IIT Bombay and currently the Chairman-India Intellectual Ventures. Misra, who has also been chairperson of IIT Council Committee for JEE examination, says, "ultimately it is all about the perception of students and their parents about institutes."

A few students have also chosen new IITs including Gandhinagar, Ropar, Indore and IIT Jodhpur. Last year, none of these institutes figured in the list of top 1,000 rankers.

Courtesy: The Economic Times

NEET | JEE

ESSENTIALS

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Unit 2

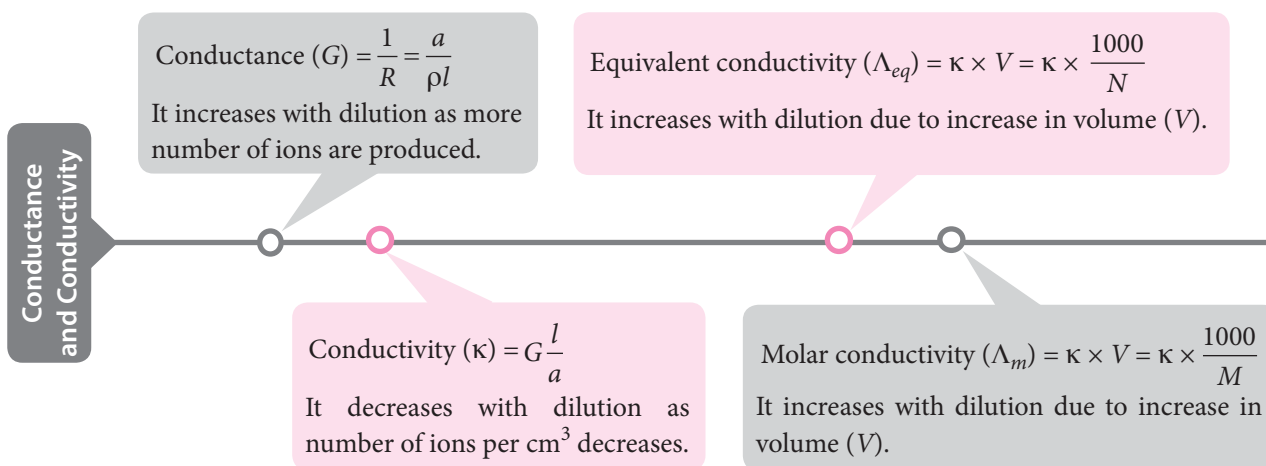
Electrochemistry Chemical Kinetics Surface Chemistry

ELECTROCHEMISTRY

- ↪ The study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.
- ↪ The commercial production of a number of metals (like Na, Mg, Ca and Al) and chemicals

(like NaOH, Cl₂, F₂), batteries and cells used in various instruments and the sensory signals sent to brain through the cells and vice versa and also the communication among different cells are based on electrochemical phenomena.

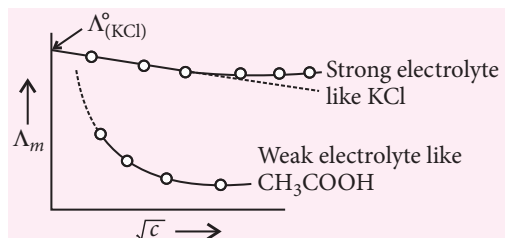
CONDUCTANCE IN ELECTROLYTIC SOLUTIONS



VARIATION OF MOLAR CONDUCTIVITY WITH CONCENTRATION

For a strong electrolyte, Λ_m increases slowly with dilution which is shown by *Debye-Huckel Onsager equation* as follows :

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



Here, Λ_m° = Molar conductivity at infinite dilution (Limiting molar conductivity)

Λ_m = Molar conductivity at V -dilution

A = Constant which depends upon nature of solvent and temperature

c = Concentration

KOHLRAUSCH'S LAW

Equivalent conductivity at infinite dilution

$$\Lambda_{eq}^\circ = \lambda_{cation}^\circ + \lambda_{anion}^\circ$$

Molar conductivity at infinite dilution,

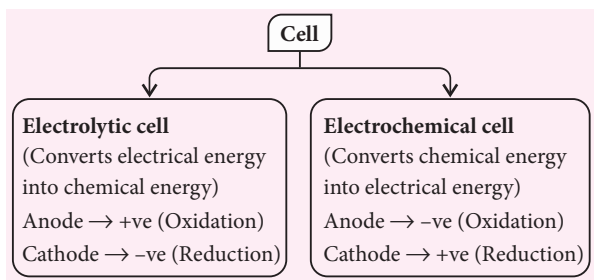
$$\Lambda_m^\circ \text{ for } A_xB_y = x\lambda_+^\circ + y\lambda_-^\circ$$

It helps in calculation of molar conductivity (Λ_m°), degree of dissociation (α) and dissociation constant (K_c) of weak electrolytes.

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ}; K_c = \frac{c\alpha^2}{1-\alpha}$$

{For reaction, $AB \rightleftharpoons A^+ + B^-$ }

TYPES OF CELLS



CELL POTENTIAL OR EMF OF A CELL

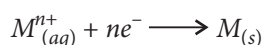
$$E_{cell}^\circ = E_{ox}^\circ (\text{anode}) + E_{red}^\circ (\text{cathode})$$

$$E_{cell}^\circ = E_{red}^\circ (\text{cathode}) - E_{red}^\circ (\text{anode}) = E_{right}^\circ - E_{left}^\circ$$

$$E_{cell}^\circ = E_{ox}^\circ (\text{anode}) - E_{ox}^\circ (\text{cathode})$$

NERNST EQUATION

For electrode reaction,



$$E_{M^{n+}/M} = E_{M^{n+}/M}^\circ - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]} (\because [M] = 1)$$

$$= E_{M^{n+}/M}^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \text{ at } 298 \text{ K}$$

For electrochemical reaction,



$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where, $E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ$ and concentrations of pure solids are taken as unity.

Equilibrium constant from Nernst equation,

At equilibrium, $E_{cell} = 0$ thus,

$$E_{cell}^\circ = \frac{2.303RT}{nF} \log K_c \text{ at } 298 \text{ K}$$

FARADAY'S LAWS OF ELECTROLYSIS

Faraday's first law of electrolysis,

$$w = Z \times I \times t$$

$$\text{where } Z = \frac{\text{Eq. wt. of substance}}{96500}$$

Faraday's second law of electrolysis,

$$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$



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Working of Lithium-ion batteries!

In a rechargeable lithium-ion, the positive electrode is typically made from a chemical compound called lithium-cobalt oxide (LiCoO_2) or, in newer batteries, from lithium iron phosphate (LiFePO_4). The negative electrode is generally made from carbon (graphite) and the electrolyte varies from one type of battery to another. When the battery is charging up, the lithium-cobalt oxide, positive electrode gives up some of its lithium ions, which move through the electrolyte to the negative, graphite electrode and remain there. The battery takes in and stores energy during this process. When the battery is discharging, the lithium ions move back across the electrolyte to the positive electrode, producing the energy that powers the battery. In both cases, electrons flow in the opposite direction to the ions around the outer circuit.

CHEMICAL KINETICS

The branch of chemistry which deals with the study of the speeds or the rates of chemical reactions, the factors affecting the rates of the reactions and the mechanism by which the reactions proceed.

RATE OF CHEMICAL REACTION

For reaction, $A \rightarrow B$

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

$$\text{Instantaneous rate} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

$$\text{Average rate of reaction} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

FACTORS AFFECTING RATE OF REACTION

Size of solid reactant decreases, rate of reaction increases.

Rate of reaction \propto Temperature

Gaseous state > Liquid state > Solid state
 → Decreasing rate of reaction

Rate of reaction \propto Concentration of reactant

A positive catalyst increases while negative catalyst decreases the rate of reaction by altering the reaction pathway and activation energy.

TYPES OF REACTIONS

- Elementary reactions : Single step reaction with no detectable intermediate.
- Complex reaction : Involves more than one elementary reactions.

Number of concepts have been put forward to characterise acids and bases like Faraday considered them as electrolytes, Liebig termed acids as compounds that can replace its hydrogen with metals. Though the three most important are Arrhenius, Bronsted-Lowry and Lewis concepts.

Arrhenius Concept

- A substance which furnishes H^+ ions when dissolved in water is an *acid* while the substance which furnishes OH^- ions is a *base*.



- Acids and bases that dissociate completely in aqueous solutions are strong acids (e.g., HCl , H_2SO_4) and strong bases (e.g., $NaOH$, KOH) while that dissociate to limited extent are weak acids (e.g., CH_3COOH , H_2CO_3) and weak bases (e.g., NH_4OH , $Al(OH)_3$).

- Many oxides of non-metals in water give H^+ ions thus, they are acidic in nature.

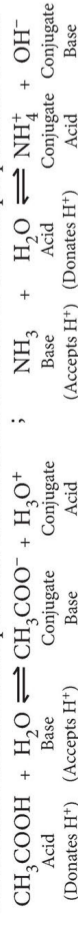


Similarly, many oxides of metals and other compounds in water give OH^- ions thus, they are basic in nature.



Bronsted - Lowry Concept

- A substance which donates proton is an *acid* and a substance which accepts proton is a *base*.



- Water is an *amphoteric* substance i.e., it can donate as well as accept the proton.

- If Bronsted acid is strong, then its conjugate base is weak and vice versa.

- The strength of acids (or bases) also depends upon the medium acting as base (or acid), e.g., HCl is neutral in benzene, since benzene does not accept proton.

- All Arrhenius acids are also Bronsted acids but all Arrhenius bases are not Bronsted bases.

Lewis Concept

- A substance which accepts electron pair is an *acid* while the substance which donates electron pair is a *base*.



- Species that can act as Lewis acids are:

- Molecules with incomplete octet of central atom e.g., BF_3 , $AlCl_3$, $BeCl_2$, etc.
- Molecules with central atom having empty *d*-orbitals e.g., SF_4 , $TiCl_4$, SiF_4 , $SnCl_4$, etc.
- All cations e.g., H^+ , Ag^+ , Cu^{2+} , etc.
- Molecules with a multiple bond between atoms of dissimilar electronegativity e.g., CO_2 , SO_2 , etc.
- Species that can act as Lewis bases are:
- Neutral molecules having at least one lone pair of electrons e.g., $\ddot{N}H_3$, $\ddot{O}H_2$, $\ddot{R}NHR_2$, etc.
- All anions e.g., CN^- , F^- , OH^- , etc.

- This concept is so general that any reaction with the formation of coordinate bond is considered to be acid-base reaction however, it is not always true.

- It explains that formation of coordinate bond is necessary for an acid-base reaction but no such bond is formed between

HCl and $NaOH$ which is an acid-base reaction.

- It does not predict the relative strength of acids and bases.
- It cannot explain the catalytic activity of acids which is due to H^+ ions. As for Lewis acid it is not necessary to give H^+ ions, many Lewis acids will not have this property.

Natural or synthetic substances which when applied on or taken into a living body affect its functioning and is used in the diagnosis, mitigation, treatment or prevention of a disease.

Analgesics

- Used to relieve pain without causing reduction of consciousness, mental confusion or other disturbances of nervous system. These are of two types:
 - Non-narcotics (non-addictive)**: These are not potent and do not cause addiction. e.g., aspirin, paracetamol, etc. They have other effects also such as antipyretic (reducing fever) and anti-blood clotting action.
 - Narcotics (addictive)**: Produce analgesia and sleep in small doses but in large doses cause coma, convulsions and may ultimately lead to death e.g., morphine, codeine, etc.

Neurologically Active Drugs

Affect the message transfer mechanism from nerve to receptor. Tranquillizers and analgesics are such type of drugs.

Antihistamines

- Diminish or abolish the effects of histamine released in the body and hence prevent from allergic reactions caused by dust, particular type of food or fabric, etc.
- Commonly used antihistamine drugs are cetirizine, maleate (avil), promethazine, etc.

Antiseptics and Disinfectants

- Antiseptics either kill or inhibit the growth of microorganisms and can be applied to the living tissues but cannot be ingested like antibiotics e.g., soframycin, iodoforn, 0.2% solution of phenol, etc.
- Disinfectants also either kill or inhibit the growth of microorganisms but can be applied to inanimate objects only i.e., floors, instruments, etc. e.g., 1% solution of phenol, 0.2-0.4 ppm Cl_2 (aq.), etc.

Antibiotics

- Produced wholly or partly by chemical synthesis and in low concentration, either kill (bactericidal drugs) or inhibit the growth of microorganisms (bacteriostatic drugs) by intervening in their metabolic processes.
- Bactericidal drugs** → Penicillin, ofloxacin, streptomycin, etc.
- Bacteriostatic drugs** → Erythromycin, tetracycline, chloramphenicol, etc.
- Classification on the basis of range of microorganisms that are affected by a certain antibiotic (called its spectrum of action).
- Broad spectrum antibiotics** - Kill or inhibit wide range of Gram-positive and Gram-negative bacteria e.g., tetracycline, vancomycin, etc.
- Narrow spectrum antibiotics** - Kill or inhibit mainly against Gram-positive or Gram-negative bacteria e.g., penicillin G.
- Sulpha drugs (e.g., sulphadiazine, sulphathiazole) are also antibiotics that are used in pneumonia, tuberculosis, etc.

Tranquillizers

- Used for the treatment of stress, fatigue, mild and severe mental diseases by inducing a sense of well-being. These are also called *psychotherapeutic drugs* e.g., chloridiazepoxide and meprobamate.
- An important class of tranquillizers are barbiturates which are used as *hypnotics* i.e., sleep producing agents e.g., luminal, amytal, etc.

Antimicrobials

- Destroy/prevent development of microbes or inhibit the pathogenic action of microbes. Antibiotics, antiseptics and disinfectants are *antimicrobials*.

Antifertility Drugs

- Used to check pregnancy in women by controlling the menstrual cycle and ovulation e.g., norethindrone, novestrol, etc.

Antacids

- Neutralize the excess acid and raise the pH to an appropriate level in stomach.
- Weak bases like $NaHCO_3$, $Mg(OH)_2$, $CaCO_3$, etc. are commonly used but metal hydroxides are better alternatives as they are insoluble thus, do not increase the pH above neutrality.
- The most effective antacids are omeprazole and lansoprazole.

MOLECULARITY AND ORDER OF A REACTION

↪ **Molecularity of a reaction** : It is the total number of species taking part in an elementary reaction and its value is a whole number only.

↪ **Order of a reaction** : It is the sum of the powers of the concentration terms of reacting species in the rate law expression and its value may be zero, fractional or an integer.

RATE LAW, INTEGRATED RATE LAW, HALF-LIFE, UNIT OF RATE CONSTANT AND GRAPH FOR THE REACTIONS OF DIFFERENT ORDERS

Order	Rate law	Integrated rate law	Half-life	Unit of rate constant	Graph
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	$\text{mol L}^{-1} \text{s}^{-1}$	$[A]$ vs t ; slope = $-k$
1	Rate = $k[A]^1$	$\ln[A]_t = -kt + \ln [A]_0$	$t_{1/2} = 0.693/k$	s^{-1}	$\ln[A]$ vs t ; slope = $-k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k [A]_0$	$\text{L mol}^{-1} \text{s}^{-1}$	$1/[A]$ vs t ; slope = k
2	Rate = $k[A][B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$	-	$\text{L mol}^{-1} \text{s}^{-1}$	$1/[A]$ vs t ; slope = k
n	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}$	$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$	$(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$	$\frac{1}{[A]^{n-1}}$ vs t ; slope = k

ARRHENIUS EQUATION

↪ $k = Ae^{-E_a/RT}$ or $\log k = \log A - \frac{E_a}{2.303RT}$

↪ For a reaction, at two different temperatures

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

where, k_1 and k_2 are the values of rate constant at temperatures T_1 and T_2 respectively.

COLLISION THEORY

↪ Reactions occur only when molecules collide with appropriate orientation and sufficient energy ($E > E_a$). Rate = $PZ_{AB}e^{-E_a/RT}$ where, P = probability or steric factor which takes into account the fact that in a collision, molecules must be properly oriented and Z_{AB} = collision frequency (*i.e.*, the no. of collisions per second per unit volume of the reaction mixture) of reactants, A and B .

Pharmacokinetic Parameters of Elimination

Pharmacokinetic studies the manner and speed with which drugs and their metabolites are eliminated by the various excretory organs.

Zero-order elimination kinetics : "Elimination of a constant quantity per unit time of the drug quantity present in the organism". The elimination is independent of the drug concentration in the body.

First order elimination kinetics : "Elimination of a constant fraction per unit time of the drug quantity present in the organism. The elimination is proportional to the drug concentration". 95% of the drugs in use at therapeutic concentrations are eliminated by first order elimination kinetics. A few substances are eliminated by zero-order elimination kinetics, because their elimination process is saturated. Examples are ethanol, phenytoin, salicylates, cisplatin, fluxetin, omeprazol.



SURFACE CHEMISTRY

ADSORPTION

↳ *Adsorption* is the phenomenon of existence of higher concentration of any particular component (*adsorbate*) at the surface of liquid or solid phase (*adsorbent*) than in the bulk.

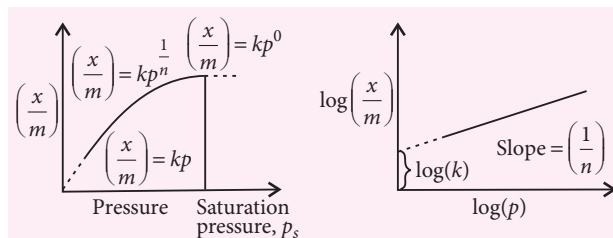
↳ Physisorption and Chemisorption

Physisorption	Chemisorption
Molecules are held by weak van der Waals' forces and it is reversible in nature.	Molecules are held by chemical bonds and it is irreversible in nature.
More easily liquefiable gases are adsorbed readily.	Gases which can react with the adsorbent show chemisorption.
Enthalpy of adsorption is low (20 - 40 kJ mol ⁻¹)	Enthalpy of adsorption is high (80 - 240 kJ mol ⁻¹)
Low temperature and large surface area are favourable.	High temperature and large surface area are favourable.
Forms multimolecular layer.	Forms unimolecular layer.

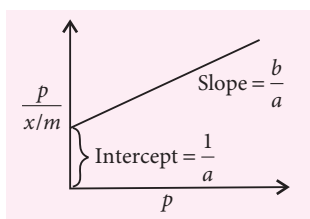
ADSORPTION ISOTHERMS

↳ **Freundlich adsorption isotherm** : It is the plot of $\frac{x \text{ (mass of adsorbent)}}{m \text{ (mass of adsorbate)}}$ vs pressure at constant temperature.

- For low pressure, $\frac{x}{m} \propto p$
 - For high pressure, $\frac{x}{m} \propto p^0$
 - For intermediate pressure, $\frac{x}{m} \propto p^{1/n} (n > 1)$
- $$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$



↳ **Langmuir adsorption isotherm** : Applicable for monolayer adsorption, $\frac{x}{m} = \frac{ap}{1+bp}$ where, a and b are constants whose values depend upon the nature of the gas adsorbed, nature of the adsorbent and temperature.



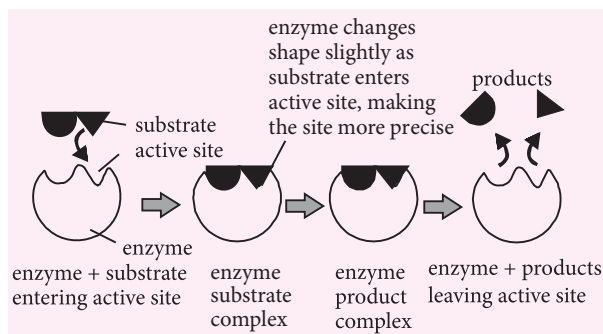
CATALYSIS

↪ **Catalysis** is the process of enhancing the rate of a reaction by a catalyst. The ability of catalysts to catalyse a particular reaction only is called *selectivity of catalysts*.

- **Homogeneous catalysis** : The process in which the reactants and the catalyst are in the same phase.
- **Heterogeneous catalysis** : The process in which

the reactants and the catalyst are in different phases.

↪ **Enzyme catalysis** : Process of catalysing all biological reactions by special catalyst called enzymes (or biochemical catalysts). Chemically, all enzymes are globular proteins.



COLLOIDS, TRUE SOLUTIONS AND SUSPENSIONS

True Solutions

- Size of particles is < 1 nm.
- Separation is not possible by filter paper or parchment membrane.
- It is transparent and homogenous.

Colloids

- Size of particles is 1 - 1000 nm.
- Separation is possible with parchment membrane.
- It is translucent and heterogenous.

Suspensions

- Size of particles is > 1000 nm.
- Separation can be done even with filter paper.
- It is opaque and heterogenous.

Multimolecular colloids

Colloidal particles are aggregates of molecules e.g., S₈, gold etc.

Macromolecular colloids

Colloidal particles are macromolecules e.g., starch, cellulose, protein, etc.

Associated colloids (Micelles)

Ions aggregate to form micelles. e.g., soaps and detergents.

Lyophilic colloids

Reversible sols, quite stable

Lyophobic colloids

Irreversible sols, not stable

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Colligative properties - Values are very low due to aggregation.

Brownian movement - Zig-zag movement of particles that stabilise colloidal sols.

Electrophoresis - Movement of colloidal particles towards opposite charged electrode under the influence of electric field. Different colloidal particles have different mobilities using this property mixture of colloids can be separated.

Tyndall effect - Scattering of light by colloidal particles.

Electrical properties - All dispersed particles of sol have same charge so, they repel each other and stabilise colloidal sol.

Coagulation - Precipitation of colloidal sol by the addition of electrolyte.

PROTECTIVE POWER AND COAGULATING POWER

↪ **Gold number** is the minimum mass (in milligrams) of the protective colloid which must be added to 10 mL of a standard red gold sol to prevent the coagulation when 1 mL of 10% solution of NaCl is added to it.

↪ Protective power $\propto \frac{1}{\text{Gold number}}$

↪ Greater the valency of coagulating ion of the electrolyte, faster is the coagulation (*Hardy-Schulze Rule*).

➤ Flocculation value $\propto \frac{1}{\text{Coagulating power}}$

EMULSIONS

↪ Colloidal system in which both the dispersed

phase and dispersion medium are liquids is called emulsion.

➤ Oil in water type : Oil is dispersed phase and water is dispersion medium *e.g.*, milk, body lotion, etc.

➤ Water in oil type : Water is dispersed phase and oil is dispersion medium *e.g.*, butter, cold cream, etc.

➤ Emulsification : Process of making an emulsion.

➤ Emulsifying agent : Used to stabilize the emulsion *e.g.*, soaps and detergents.

➤ Demulsification : Separating the two components of an emulsion. Methods used are boiling, freezing, changing pH.



Applications of Surface Chemistry

The Nobel Prize in Chemistry for 2007 was awarded to Gerhard Ertl for his studies of chemical processes in solid surfaces. Surface chemistry, a science that is really important for the chemical industry. It improves understanding of a variety of processes, including iron rusting, fuel cells functioning and working of the catalysts in our cars. Chemical reactions on catalytic surfaces are really important for a lot of industrial operations, including the production of artificial fertilizers. Surface chemistry can even provide explanation of the ozone layer destruction, with vital steps in the reaction taking place on the surfaces of small crystals of ice in the stratosphere. The semiconductor industry also greatly depends on knowledge of surface chemistry.

SPEED PRACTICE

- The quantity of electricity required to liberate 112 cm^3 of hydrogen at STP from acidified water is
(a) 0.1 faraday (b) 96500 coulomb
(c) 965 coulomb (d) 10 faraday.
- Addition of lyophilic sols. to lyophobic colloid, forms
(a) a protective film around the dispersed phase
(b) a protective film around the dispersion medium
(c) an aerosol
(d) true solution.
- For the following electrochemical cell at 298 K,
 $\text{Pt}_{(s)}|\text{H}_{2(g)}(1 \text{ bar})|\text{H}^+_{(aq)}(1 \text{ M})||\text{M}^{4+}_{(aq)}, \text{M}^{2+}_{(aq)}|\text{Pt}_{(s)}$
 $E_{\text{cell}} = 0.092 \text{ V}$ when $\frac{[\text{M}^{2+}_{(aq)}]}{[\text{M}^{4+}_{(aq)}]} = 10^x$
Given : $E^\circ_{\text{M}^{4+}/\text{M}^{2+}} = 0.151 \text{ V}$; $2.303 \frac{RT}{F} = 0.059 \text{ V}$
The value of x is
(a) -2 (b) -1
(c) 1 (d) 2 (JEE Advanced 2016)
- The coagulation of 10 mL of a colloidal sol of gold is completely prevented by addition of 0.25 g of a substance X to it before adding 1 mL of 10% NaCl solution. The gold number of X is
(a) 25 (b) 0.25
(c) 2.5 (d) 250
- A cell is containing two H electrodes. The negative electrode is in contact with a solution of 10^{-6} M H^+ ions. The e.m.f. of the cell is 0.118 V at 25°C . What is the $[\text{H}^+]$ at positive electrode?
(a) 10^{-4} M (b) 10^{-6} M
(c) 10^{-2} M (d) 10^{-8} M
- The addition of a catalyst during a chemical reaction alters which of the following quantities?
(a) Enthalpy (b) Activation energy
(c) Entropy (d) Internal energy
(NEET 2016)
- Faraday's laws of electrolysis will fail when
(a) temperature is increased
(b) inert electrodes are used
(c) a mixture of electrolytes is used
(d) in none of these cases.
- Two faradays of electricity are passed through a solution of CuSO_4 . The mass of copper deposited at the cathode is (at. mass of Cu = 63.5 amu)
(a) 2 g (b) 127 g
(c) 0 g (d) 63.5 g (JEE Main 2015)
- Bleeding is stopped by the application of ferric chloride. This is because
(a) the blood starts flowing in the opposite direction
(b) the blood reacts and a solid is formed which seals the blood vessel
(c) the blood is coagulated and the blood vessels are sealed
(d) the ferric chloride seals the blood vessel.
- Which property of colloidal solution is independent of charge on the colloidal particles?
(a) Electro-osmosis (b) Tyndall effect
(c) Coagulation (d) Electrophoresis
(AIPMT 2015)
- For the elementary reaction $M \rightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M . The order of the reaction with respect to M is
(a) 4 (b) 3
(c) 2 (d) 1 (JEE Advanced 2014)
- A hypothetical reaction, $A_2 + B_2 \longrightarrow 2AB$ follows the mechanism as given below;
 $A_2 \rightleftharpoons A + A \dots\dots(\text{fast})$
 $A + B_2 \longrightarrow AB + B \dots\dots(\text{slow})$
 $A + B \longrightarrow AB \dots\dots(\text{fast})$
The order of the overall reaction is
(a) 2 (b) 1
(c) - (d) zero.
- Higher order (>3) reactions are rare due to
(a) shifting of equilibrium towards reactants due to elastic collisions
(b) loss of active species on collision
(c) low probability of simultaneous collision of all the reacting species

(d) increase in entropy and activation energy as more molecules are involved.

(JEE Main 2015)

14. Which one of the following characteristics is associated with adsorption?

- (a) ΔG and ΔH are negative but ΔS is positive.
 (b) ΔG and ΔS are negative but ΔH is positive.
 (c) ΔG is negative but ΔH and ΔS are positive.
 (d) ΔG , ΔH and ΔS all are negative. (NEET 2016)

15. A student made the following observations in the laboratory :

- (i) Clean copper metal did not react with 1 molar $\text{Pb}(\text{NO}_3)_2$ solution.
 (ii) Clean lead metal dissolved in a 1 molar AgNO_3 solution and crystals of Ag metal appeared.
 (iii) Clean silver metal did not react with 1 molar $\text{Cu}(\text{NO}_3)_2$ solution.

The order of decreasing reducing character of the three metals is

- (a) Cu, Pb, Ag (b) Cu, Ag, Pb
 (c) Pb, Cu, Ag (d) Pb, Ag, Cu

16. For the non-stoichiometric reaction :

$2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial concentration [A]	Initial concentration [B]	Initial rate of formation of C ($\text{mol L}^{-1}\text{s}^{-1}$)
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is

- (a) $\frac{dC}{dt} = k[A]$ (b) $\frac{dC}{dt} = k[A][B]$
 (c) $\frac{dC}{dt} = k[A]^2[B]$ (d) $\frac{dC}{dt} = k[A][B]^2$

(JEE Main 2014)

17. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is

- (a) second
 (b) more than zero but less than first
 (c) zero
 (d) first. (AIPMT 2014)

18. Given below are the half-cell reactions :

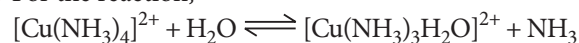


The E° for $3\text{Mn}^{2+} \longrightarrow \text{Mn} + 2\text{Mn}^{3+}$ will be

- (a) -0.33 V ; the reaction will occur
 (b) -2.69 V ; the reaction will not occur
 (c) -2.69 V ; the reaction will occur
 (d) -0.33 V ; the reaction will not occur.

(JEE Main 2014)

19. For the reaction,



the net rate of reaction at any time is given by :

$$\text{Net rate} = 2.0 \times 10^{-4} [[\text{Cu}(\text{NH}_3)_4]^{2+}] - 3.0 \times 10^5 [[\text{Cu}(\text{NH}_3)_3\text{H}_2\text{O}]^{2+}][\text{NH}_3]$$

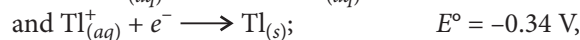
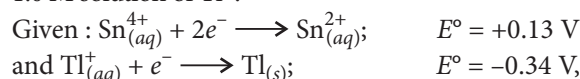
Then correct statement is (are)

- (a) rate constant for forward reaction = 2×10^{-4}
 (b) rate constant for backward reaction = 3×10^5
 (c) equilibrium constant for the reaction = 6.6×10^{-10}
 (d) all of these.

20. The pressure of H_2 required to make the potential of H_2 -electrode zero in pure water at 298 K is

- (a) 10^{-10} atm (b) 10^{-4} atm
 (c) 10^{-14} atm (d) 10^{-12} atm (NEET 2016)

21. A galvanic cell is constructed as follows. A half-cell consists of a platinum wire immersed in a solution containing 1.0 M of Sn^{2+} and 1.0 M of Sn^{4+} , and another half-cell has a thallium rod immersed in a 1.0 M solution of Tl^+ .



What is the cell voltage if the Tl^+ concentration is increased tenfold?

- (a) 0.411 V (b) 4.101 V
 (c) 0.492 V (d) 0.222 V

22. The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞ , respectively. The correct relationship between λ_C and λ_∞ is given as (where, the constant B is positive)

- (a) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$ (b) $\lambda_C = \lambda_\infty + (B)C$
 (c) $\lambda_C = \lambda_\infty - (B)C$ (d) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$

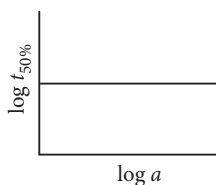
(JEE Main 2014)

23. In a second order reaction, when the concentration of both the reactants are equal, the reaction is completed 20% in 500 s. How long would it take for the reaction to go to 60% completion?
 (a) 3000 s (b) 5000 s
 (c) 1000 s (d) 2000 s
24. When 0.1 mol MnO_4^{2-} is oxidised the quantity of electricity required to completely oxidise MnO_4^{2-} is
 (a) 69500 C (b) 2×96500 C
 (c) 9650 C (d) 96.50 C (AIPMT 2014)
25. Resistance of 0.2 M solution of an electrolyte is 50 Ω . The specific conductance of the solution is 1.4 S m^{-1} . The resistance of 0.5 M solution of the same electrolyte is 280 Ω . The molar conductivity of 0.5 M solution of the electrolyte in $\text{S m}^2 \text{ mol}^{-1}$ is
 (a) 5×10^2 (b) 5×10^{-4}
 (c) 5×10^{-3} (d) 5×10^3

(JEE Main 2014)

26. Consider the following reactions at 300 K.
 $A \longrightarrow B$ (uncatalysed reaction)
 $A \xrightarrow{\text{catalyst}} B$ (catalysed reaction)
 The activation energy is lowered by $8.314 \text{ kJ mol}^{-1}$ for the catalysed reaction. The rate of this reaction is
 (a) 15 times (b) 38 times
 (c) 22 times (d) 28 times.
27. The rate of first-order reaction is $0.04 \text{ mol L}^{-1} \text{ s}^{-1}$ at 10 s and $0.03 \text{ mol L}^{-1} \text{ s}^{-1}$ at 20 s after initiation of the reaction. The half-life period of the reaction is
 (a) 44.1 s (b) 54.1 s
 (c) 24.1 s (d) 34.1 s (NEET 2016)

28. A graph plotted between $\log t_{50\%}$ vs \log concentration is a straight line. What conclusion can you draw from this graph?



- (a) $n = 1; t_{1/2} = \frac{1}{x \times a}$ (b) $n = 2; t_{1/2} = \frac{1}{a}$
 (c) $n = 1; t_{1/2} = \frac{0.693}{k}$ (d) None of these
29. According to Langmuir adsorption isotherm the amount of gas adsorbed at very high pressure
 (a) reaches a constant limiting value
 (b) goes on increasing with pressure
 (c) goes on decreasing with pressure
 (d) increases first and decreases later with pressure.

30. Which of the following is correct?
 (a) Total collision rate \propto mean speed \propto absolute temperature
 (b) Total collision rate $\propto \frac{1}{\text{mean speed}} \propto \frac{1}{\text{absolute temperature}}$
 (c) Total collision rate \propto mean speed \propto (absolute temperature) $^{1/2}$
 (d) Total collision rate \propto (mean speed) $^2 \propto$ (absolute temperature) 3

SOLUTIONS

1. (c): $\text{H}_2\text{O} \longrightarrow 2\text{H}^+ + \text{O}^{2-}$
 At cathode: $2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$
 $22,400 \text{ cm}^3$ of H_2 is released from = $2 \times 96500 \text{ C}$
 $\therefore 112 \text{ cm}^3$ of H_2 is released from

$$= \frac{2 \times 96500}{22400} \times 112 = 965 \text{ C}$$
2. (a)
3. (d): At anode: $\text{H}_{2(g)} \rightarrow 2\text{H}^+_{(aq)} + 2e^-$
 At cathode: $\text{M}^{4+}_{(aq)} + 2e^- \rightarrow \text{M}^{2+}_{(aq)}$

$$\text{H}_{2(g)} + \text{M}^{4+}_{(aq)} \rightarrow \text{M}^{2+}_{(aq)} + 2\text{H}^+_{(aq)}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{M}^{2+}][\text{H}^+]^2}{[\text{M}^{4+}]}$$

$$0.092 = \left(E^\circ_{\text{M}^{4+}/\text{M}^{2+}} - E^\circ_{\text{H}^+/\text{H}_2} \right) - \frac{0.059}{2} \log(10^x [\text{H}^+]^2)$$

$$0.092 = (0.151 - 0) - \frac{0.059}{2} \log(10^x \times 1^2)$$

$$0.092 = 0.151 - 0.0295 \log 10^x$$

$$0.0295 \log 10^x = 0.151 - 0.092$$

$$\log 10^x = \frac{0.059}{0.0295} = 2$$

$$10^x = \text{Antilog } 2 = 10^2 \therefore x = 2$$
4. (d): 0.25 g = 250 mg
5. (a): At anode: $\text{H} \longrightarrow \text{H}^+ + e^-$
 At cathode: $\text{H}^+ + e^- \longrightarrow \text{H}$
 Given that, $E_{\text{cell}} = 0.118 \text{ V}$; $[\text{H}^+]_{\text{anode}} = 10^{-6} \text{ M}$
 $E^\circ_{\text{cell}(\text{H}^+/\text{H})} = 0$; $n = 1$
 We know,
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{H}^+]_{\text{Anode}}}{[\text{H}^+]_{\text{Cathode}}}$$

$$\therefore 0.118 = 0 - \frac{0.059}{1} \log \frac{10^{-6}}{[\text{H}^+]_{\text{Cathode}}}$$

$$\text{or } \log \frac{10^{-6}}{[\text{H}^+]_{\text{Cathode}}} = -2 \Rightarrow \frac{10^{-6}}{[\text{H}^+]_{\text{Cathode}}} = 10^{-2}$$

$$\text{or } [\text{H}^+]_{\text{Cathode}} = \frac{10^{-6}}{10^{-2}} = 10^{-4} \text{ M}$$

6. (b): A catalyst provides an alternate path to the reaction which has lower activation energy.
7. (d)
8. (d): $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$
2 F charge deposit 1 mol of Cu *i.e.*, 2 F of electricity deposit 63.5 g mass of Cu at the cathode.
9. (c): Fe^{3+} ion coagulates negative sol particles of blood and seals the cut.

10. (b): Tyndall effect is scattering of light by colloidal particles which is independent of charge on them.

11. (b): $M \rightarrow N$
 $r = k[M]^x$... (i)
 $8r = k[2M]^x$... (ii)

On dividing eqn. (ii) by (i), we get
 $8 = (2)^x \Rightarrow (2)^3 = (2)^x \Rightarrow x = 3$

12. (c): For slow step,

$$r = k[A][B_2]$$

and $K_c = \frac{[A][A]}{[A_2]}$ or $[A] = K_c^{1/2}[A_2]^{1/2}$

Thus, $r = k \cdot K_c^{1/2}[A_2]^{1/2}[B_2]$
 $= k_1[A_2]^{1/2}[B_2]$ $\{k_1 = k \cdot K_c^{1/2}\}$

Hence, order is $\frac{3}{2}$.

13. (c): The reactions of higher order are very rare because of the less chances of the molecules to come together simultaneously and collide.
14. (d): As the molecules of the adsorbate are held on the surface of the solid adsorbent, entropy decreases *i.e.*, $\Delta S = -ve$.
As $\Delta G = \Delta H - T\Delta S$
For the adsorption to occur, $\Delta G = -ve$ and it is possible only if $\Delta H = -ve$.

15. (c): From observations (i), (ii) and (iii), reducing character of metals are $\text{Pb} > \text{Cu}$, $\text{Pb} > \text{Ag}$ and $\text{Cu} > \text{Ag}$. Hence, for the three metals it is $\text{Pb} > \text{Cu} > \text{Ag}$.

16. (a): For the reaction, $2A + B \rightarrow C + D$

$$\text{Rate of reaction} = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

Now, rate of reaction, $\frac{d[C]}{dt} = k[A]^x[B]^y$

From table,

$$1.2 \times 10^{-3} = k(0.1)^x (0.1)^y \quad \dots(i)$$

$$1.2 \times 10^{-3} = k(0.1)^x (0.2)^y \quad \dots(ii)$$

$$2.4 \times 10^{-3} = k(0.2)^x (0.1)^y \quad \dots(iii)$$

On dividing equation (i) by (ii), we get

$$\frac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k(0.1)^x (0.1)^y}{k(0.1)^x (0.2)^y} \Rightarrow 1 = \left(\frac{1}{2}\right)^y \Rightarrow y = 0$$

On dividing equation (i) by (iii), we get

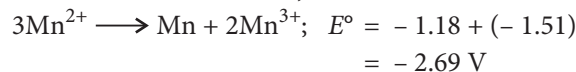
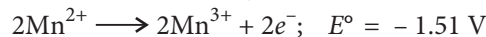
$$\frac{1.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \frac{k(0.1)^x (0.1)^y}{k(0.2)^x (0.1)^y} \Rightarrow \left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^x \Rightarrow x = 1$$

Hence, $\frac{d[C]}{dt} = k[A]^1[B]^0 = k[A]$

17. (d): Half-life period of a first order reaction is independent of initial concentration,

$$t_{1/2} = \frac{0.693}{k}$$

18. (b): Overall reaction :



As E° is negative, the reaction will not occur.

19. (d): Net rate of reaction = rate of forward reaction - rate of backward reaction
 $= K_f[\text{reactant}] - K_b[\text{product}]$

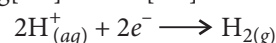
On comparing this relation with given equation, we get, $K_f = 2.0 \times 10^{-4}$, $K_b = 3.0 \times 10^5$

Also, $K_c = \frac{K_f}{K_b}$ at equilibrium

$$K_c = \frac{\times}{\times} = 6.6 \times 10^{-10}$$

20. (c): pH = 7 for water.

$$-\log[\text{H}^+] = 7 \Rightarrow [\text{H}^+] = 10^{-7}$$



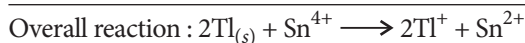
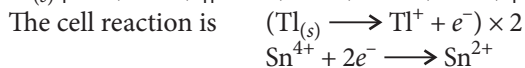
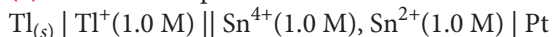
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$0 = 0 - \frac{0.0591}{2} \log \frac{P_{\text{H}_2}}{(10^{-7})^2}$$

$$\log \frac{P_{\text{H}_2}}{(10^{-7})^2} = 0 \Rightarrow \frac{P_{\text{H}_2}}{(10^{-7})^2} = 1 \quad [\because \log 1 = 0]$$

$$P_{\text{H}_2} = 10^{-14} \text{ atm}$$

21. (a): The cell is represented as



$$E = (E^\circ_{\text{Right}} - E^\circ_{\text{Left}}) - \frac{0.0592}{2} \log \frac{[\text{Tl}^+]^2 [\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}$$

$$= 0.47 \text{ V} - 0.0296 \log (10)^2$$

[∵ Tl concentration increases tenfold]

$$= 0.47 - 0.0592 = 0.411 \text{ V}$$

22. (d): According to Debye–Hückel's theory, for a strong electrolyte (like NaCl),

$$\lambda_C = \lambda_\infty - (B)\sqrt{C}$$

23. (a): In first case,

Given that, $t = 500 \text{ s}$; $a = 100$

$$a - x = 80\% \text{ of } 100 = 100 \times \frac{80}{100} = 80$$

$$\text{For second order reaction, } k = \frac{1}{t \times a} \cdot \frac{x}{a - x}$$

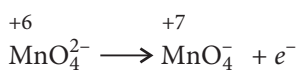
$$= \frac{1}{500 \times 100} \times \frac{20}{80} = 5 \times 10^{-6}$$

In second case, $a = 100$

$$a - x = 40\% \text{ of } 100 = 100 \times \frac{40}{100} = 40$$

$$\therefore t = \frac{1}{k \times a} \cdot \frac{x}{a - x} = \frac{1}{5 \times 10^{-6} \times 100} \times \frac{60}{40} = 3000 \text{ s}$$

24. (c): The oxidation reaction is



0.1 mol 0.1 mol

$$Q = 0.1 \times F = 0.1 \times 96500 \text{ C} = 9650 \text{ C}$$

25. (b): Case I: $C = 0.2 \text{ M}$, $R = 50 \Omega$, $\kappa = 1.4 \text{ S m}^{-1}$

$$\kappa = \frac{l}{A} \cdot \frac{1}{R} \text{ or } 1.4 = \frac{l}{A} \cdot \frac{1}{50}$$

$$\Rightarrow \frac{l}{A} = 1.4 \times 50 = 70 \text{ m}^{-1}$$

Case II: $\frac{l}{A} = 70 \text{ m}^{-1}$, $C = 0.5 \text{ M}$, $R = 280 \Omega$,

$$R = \rho \frac{l}{A} \text{ or } \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} \Rightarrow \frac{1}{\rho} = \frac{1}{280} \times 70$$

$$\kappa = \frac{1}{\rho} = 0.25 \text{ S m}^{-1}$$

$$\text{Now, } \Lambda_m = \kappa \times \frac{1000}{C}$$

If molarity is in mol L^{-1} , then

$$\begin{aligned} \Lambda_m (\text{S m}^2 \text{ mol}^{-1}) &= \frac{\kappa (\text{S m}^{-1})}{1000 \text{ L m}^{-3} \times \text{Molarity} (\text{mol L}^{-1})} \\ &= \frac{0.25 \text{ S m}^{-1}}{1000 \text{ L m}^{-3} \times 0.5 \text{ mol L}^{-1}} = 5 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1} \end{aligned}$$

$$26. \text{ (d): } k_{\text{uncat}} = A e^{-\frac{E}{RT}} \quad \dots \text{(i)}$$

$$k_{\text{cat}} = A e^{-\frac{E}{RT}} \quad \dots \text{(ii)}$$

From (i) and (ii)

$$\frac{k}{k_{\text{cat}}} = \frac{e^{-\frac{E}{RT}}}{e^{-\frac{E}{RT}}} = e^{\frac{-E}{RT}}$$

$$\frac{k}{k_{\text{cat}}} = e^{-\frac{E}{RT}} \text{ or } \frac{k_{\text{cat}}}{k} = e^{\frac{E}{RT}} = e^{3.33} \approx 28$$

27. (c): For a first order reaction, $A \rightarrow \text{Products}$ and for concentration of the reactant at two different times,

$$k = \frac{2.303}{t_2 - t_1} \log \frac{[A]_1}{[A]_2}$$

$$\therefore k = \frac{2.303}{t_2 - t_1} \log \frac{(\text{rate})_1}{(\text{rate})_2} \quad (\because \text{rate} \propto [A])$$

$$k = \frac{2.303}{(20 - 10)} \log \left(\frac{0.04}{0.03} \right) = 0.0287 \text{ sec}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287 \text{ sec}^{-1}} = 24.14 \text{ sec}$$

28. (c): $t_{1/2} \propto (a)^{(1-n)}$ or $t_{1/2} = z \cdot (a)^{(1-n)}$

$$\therefore \log t_{1/2} = \log z + (1-n)(\log a)$$

It is straight line equation and hence,

$$\text{slope} = 1 - n = 0 \Rightarrow n = 1$$

29. (a): Langmuir adsorption isotherm is applicable for monolayer adsorption which fails at high pressure because the mass adsorbed reaches a constant value when the adsorbed surface is completely covered by a unimolecular layer of gases.

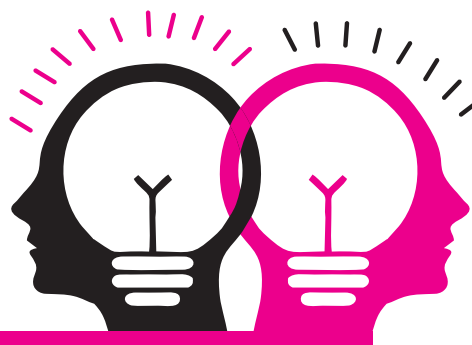
30. (c): Collision rate (z) = $N_a N_b \sigma_{ab} \sqrt{\frac{k_B T}{\pi \mu_{ab}}}$

where, $\sqrt{\frac{k_B T}{\pi \mu_{ab}}}$ = mean speed

N_a and N_b are number of molecules of 'a' and 'b'.



EXAMINER'S MIND CLASS XII



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

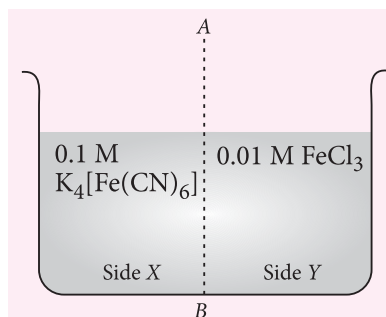
Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

SOLUTIONS

SECTION - I

Only One Option Correct Type

- Two liquids *A* and *B* form an ideal solution at 300 K, the vapour pressure of a solution containing 1 mol of *A* and 3 mol of *B* is 550 mm Hg. At the same temperature if one mol *B* is added to this solution, the vapour pressure of the solution increases by 10 mm Hg. The vapour pressure of pure *A* is
(a) 600 mm Hg
(b) 100 mm Hg
(c) 400 mm Hg
(d) 500 mm Hg
- An aqueous solution of 6.3 g oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is
(a) 40 mL
(b) 20 mL
(c) 10 mL
(d) 4 mL
- FeCl_3 on reaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$ in aqueous solution gives blue colour. These are separated by a semipermeable membrane *AB* as shown. Due to osmosis there is
(a) blue colour formation in side *X*
(b) blue colour formation in side *Y*
(c) blue colour formation in both of the sides *X* and *Y*
(d) no blue colour formation.
- An aqueous solution of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ of strength 34.2 g/L has an osmotic pressure of 2.38 atmospheres at 17°C. For an aqueous solution of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$ to be isotonic with this solution, its strength would be
(a) 34.2 g/L
(b) 17.1 g/L
(c) 18.0 g/L
(d) 36.0 g/L
- Relative decrease in vapour pressure of an aqueous glucose dilute solution is found to be 0.018. Hence,



elevation in boiling point is : (It is given that 1 molal aqueous urea solution boils at 100.54°C at 1 atm pressure)

- (a) 0.018 K (b) 0.18 K
(c) 0.54 K (d) 0.03 K

6. Plot of $\frac{1}{X_A}$ vs $\frac{1}{Y_A}$ (X_A mole fraction of A in liquid and Y_A in vapour) is linear whose slope and intercept respectively are given :

- (a) $p_B^\circ/p_A^\circ, \frac{p_B^\circ - p_A^\circ}{p_B^\circ}$ (b) $p_A^\circ - p_B^\circ, \frac{p_A^\circ - p_B^\circ}{p_B^\circ}$
(c) $p_A^\circ/p_B^\circ, \frac{p_B^\circ - p_A^\circ}{p_B^\circ}$ (d) $p_B^\circ - p_A^\circ, \frac{p_A^\circ - p_B^\circ}{p_B^\circ}$

7. The molarity of solution of CaCl_2 if on chemical analysis it is found that 200 mL of CaCl_2 contains 3.01×10^{22} Cl^- ions is

- (a) 40 M (b) 3.01 M
(c) 0.125 M (d) 0.250 M

8. An ideal solution is made from 5 moles of benzene and 3.25 moles of toluene. At 298 K, the vapour pressure of pure benzene and pure toluene are 96.4 torr and 28.9 torr. Total vapour pressure of the solution is

- (a) 760 torr (b) 96.4 torr
(c) 28.9 torr (d) 69.8 torr

9. Two elements A and B form compounds of formula AB_2 and AB_4 . When dissolved in 20.0 g of benzene 1.0 g of AB_2 lowers freezing point by 2.3°C whereas 1.0 g of AB_4 lowers freezing point by 1.3°C. The K_f for benzene is 5.1. The atomic masses of A and B are

- (a) 25, 42 (b) 42, 25
(c) 52, 48 (d) 48, 52

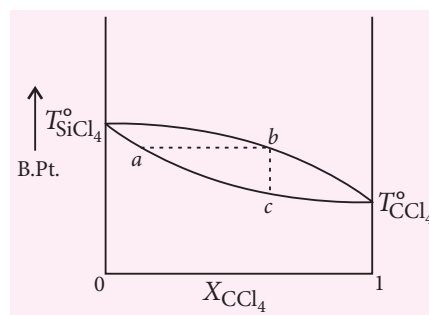
10. A dry air is passed through the solution, containing the 10 g of solute and 90 g of water and then it is passed through pure water. There is depression in weight of solution by 2.5 g and in weight of pure solution by 0.05 g. The molecular weight of solute is

- (a) 25 g mol^{-1} (b) 50 g mol^{-1}
(c) 100 g mol^{-1} (d) 180 g mol^{-1}

SECTION - II

More than One Options Correct Type

11. The diagram given below depicts the boiling point as the function of composition of the mixture of CCl_4 and SiCl_4 . Which of the following statements about the diagram is/are true?



- (a) The point *a* presents the composition of solution and the point *b* that of the vapour in equilibrium.
(b) The proportion of CCl_4 in the solution is smaller than that in the vapour in equilibrium.
(c) *bc* represents the condensation of the vapour.
(d) The point *c* represents the composition of solution and the point *b* that of the vapour in equilibrium.
12. On the basis of information given below mark the incorrect option.
- (I) In bromoethane and chloroethane mixture intermolecular interactions of $A-A$ and $B-B$ type are nearly same as $A-B$ type interactions.
(II) In ethanol and acetone mixture $A-A$ or $B-B$ type intermolecular interactions are stronger than $A-B$ type interactions.
(III) In chloroform and acetone mixture $A-A$ or $B-B$ type intermolecular interactions are weaker than $A-B$ type interactions.
- (a) Solution (II) and (III) will follow Raoult's law.
(b) Solution (I) will follow Raoult's law.
(c) Solution (II) will show negative deviation from Raoult's law.
(d) Solution (II) will show positive deviation from Raoult's law.
13. Solutions showing negative deviations from Raoult's law include
- (a) ethyl alcohol + water
(b) nitric acid + water
(c) acetone + carbon disulphide
(d) acetone + aniline.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

The partial vapour pressure of any volatile component of an ideal solution is equal to the vapour pressure of pure component multiplied by the mole fraction of the component in the solution.

14. At a given temperature, total vapour pressure (in torr) of a mixture of volatile components *A* and *B* is given by $p = 120 - 75X_B$ where, X_B is mole fraction of the component *B* in mixture.

Thus, vapour pressures of pure *A* and *B* respectively (in torr), are

- (a) 120, 75 (b) 120, 195
(c) 120, 45 (d) 75, 45

15. Total vapour pressure of the distillate of 1 mole *A* and 2 moles *B*, is

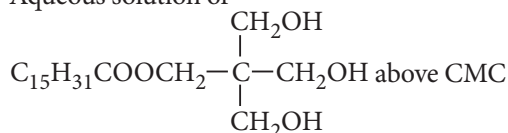
- (a) 70 torr (b) 55 torr
(c) 120 torr (d) 75 torr

Paragraph for Questions 16 and 17

Measure of colligative properties of dilute solutions of many substances may be used to determine their molecular masses. However, in some cases the calculated values differ considerably from the normal values. Their departure from the normal values is owing to the change of molecular state of the solute in the solution. The ratio of normal molecular mass to the observed value called van't Hoff factor, *i*, reflects the kind of change of molecular state of the dissolved substance.

16. Which of the following substances will not show the abnormal colligative properties in solutions?

- (a) Aqueous solution of sodium oleate
(b) Aqueous solution of



- (c) Phenol in benzene
(d) Aqueous solution of thiourea

17. Molal cryoscopic constant of water is $1.80 \text{ K kg mol}^{-1}$. A solution containing 6.00 g of pure acetic acid in 1 kg of water will show a depression of freezing point to be

- (a) 0.18 K (b) 0.36 K
(c) slightly greater than 0.18 K
(d) slightly less than 0.36 K

SECTION - IV

Matching List Type

18. Solubility of a solid solute into water increases as the temperature is raised. Match the processes listed in List I with the changes in appropriate properties listed in List II. (where *m* = molality) and select the correct answer using the code given below the lists :

List I

- P. Gas + Water \rightarrow Solution
Q. Solid + Water \rightarrow Solution
R. Saturated solution + Solid solute
S. Supersaturated solution + Solid solute

List II

1. $\Delta H > 0, \Delta S > 0$
2. $\Delta H = 0, \Delta m = 0$
3. $\Delta H < 0, \Delta m < 0$
4. $\Delta H < 0, \Delta S < 0$

P Q R S

- (a) 1 2 3 4
(b) 3 1 2 4
(c) 4 1 2 3
(d) 2 1 3 4

19. Match the entries of List I with appropriate entries of List II and select the correct answer using the code given below the lists :

List I

- P. 0.91% NaCl solution in contact with RBCs
Q. 1.25% NaCl solution in contact with RBS
R. 0.75% NaCl solution in contact with RBCs
S. 5.85% NaCl solution in contact with a glass wall

List II

1. Hypertonic solution
2. Hypotonic solution
3. Isotonic solution
4. Normal solution

P Q R S

- (a) 1 2 3 4
(b) 3 1 2 4
(c) 4 1 2 3
(d) 2 1 3 4

SECTION - V

Assertion Reason Type

20. **Assertion** : The solubility of a gas in a liquid increases with increase of pressure.

Reason : The solubility of a gas in a liquid is directly proportional to the pressure of the gas.

21. **Assertion** : One molar aqueous solution has always higher concentration than one molal.

Reason : The molality of a solution depends upon the density of the solution whereas molarity does not.

22. **Assertion** : Azeotropic mixtures are formed only by non-ideal solutions.

Reason : Boiling point of an azeotrope is either higher than both the components or lower than both the components.

SECTION - VI

Integer Value Correct Type

23. Iron (III) sulphate is 50% ionised in aqueous solution at 298 K. What is van't Hoff factor?
24. K_f of water is $1.86 \text{ K kg mol}^{-1}$. If your automobile's radiator holds 1.0 kg of water, the gram of ethylene

glycol ($\text{C}_2\text{H}_6\text{O}_2$) that must be added to get the freezing point of the solution lowered to -2.8°C is $(90 + x)$ g. The value of x is

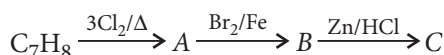
25. 29.2% (w/w) HCl stock solution has a density of 1.25 g mL^{-1} . The molecular weight of HCl is 36.5 g mol^{-1} . The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is

HALOALKANES AND HALOARENES

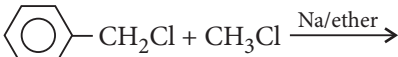

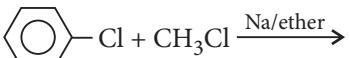
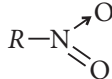
SECTION - I

Only One Option Correct Type

1. Given :



The compound C is

- (a) *o*-bromotoluene (b) *m*-bromotoluene
(c) *p*-bromotoluene
(d) 3-bromo-2,4,6-trichlor.
2. Which is not the Wurtz-Fittig reaction?
- (a)  $\xrightarrow{\text{Na/ether}}$
- (b)  $\xrightarrow{\text{Na/ether}}$
- (c)  $\xrightarrow{\text{Na/ether}}$
- (d) None of these
3. Which of the following pairs is/are correctly matched?
- | Reaction | Product |
|---------------------------------|---|
| I. $\text{RX} + \text{AgCN}$ | RNC |
| II. $\text{RX} + \text{KCN}$ | RCN |
| III. $\text{RX} + \text{KNO}_2$ |  |
| IV. $\text{RX} + \text{AgNO}_2$ | R-O-N=O |
- (a) Only I (b) I and II
(c) III and IV (d) I, II, III and IV

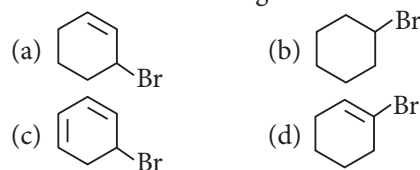
4. Boiling points of alkyl chloride, alkyl iodide have been compared with alkane.

		Boiling point
<i>n</i> -butyl chloride	$(92.5 \text{ g mol}^{-1})$	78.4°C
<i>n</i> -hexane	$(86.2 \text{ g mol}^{-1})$	68.7°C
methyl iodide	(142 g mol^{-1})	42.5°C
<i>n</i> -decane	(142 g mol^{-1})	164°C

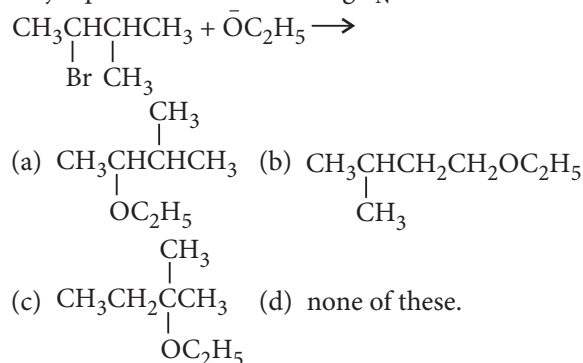
Boiling point of *n*-hexane is almost same as of *n*-butyl chloride (of same molar mass) while boiling point of *n*-decane is higher than that of methyl iodide (of same molar mass). It is due to

- (a) greater molecular volumes of alkanes than alkyl iodide
(b) compensation of polar effects and molecular volumes in alkyl chloride and alkanes
(c) both (a) and (b)
(d) none of these.

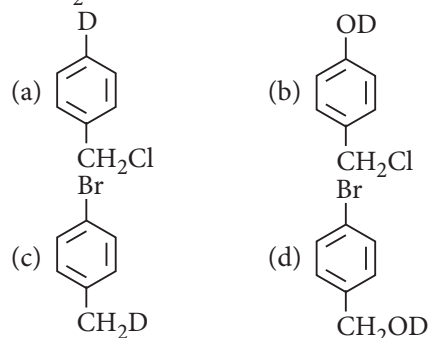
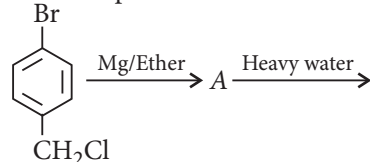
5. Which of the following is fast de-brominated?



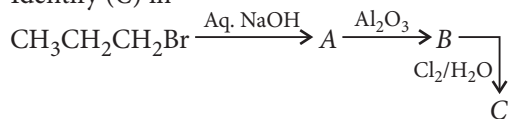
6. Major product of the following $\text{S}_{\text{N}}1$ reaction is



7. The final product obtained in the reaction

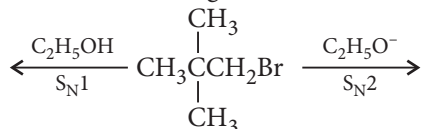


8. Identify (C) in



- (a) $\text{CH}_3\text{CHOHCH}_2\text{Cl}$
 (b) $\text{CH}_3\text{CHClCH}_2\text{Cl}$
 (c) mixture of $\text{CH}_3\text{CHCl}\cdot\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CHOHCH}_2\text{Cl}$
 (d) $\text{CH}_3\text{CH}_2\text{ClCH}_2\text{OH}$

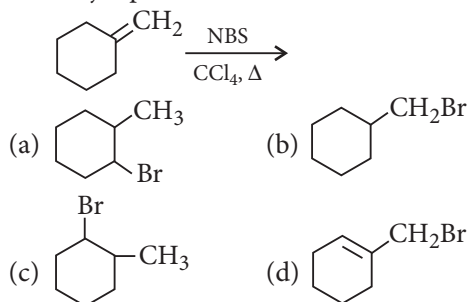
9. Consider the following reaction,



$(\text{CH}_3)_3\text{CCH}_2\text{Br}$ shows $\text{S}_{\text{N}}2$ reaction with $\text{C}_2\text{H}_5\text{O}^-$ and $\text{S}_{\text{N}}1$ reaction with $\text{C}_2\text{H}_5\text{OH}$ as given above. Select the incorrect statement.

- (a) Product obtained by $\text{S}_{\text{N}}2$ reaction has inverted configuration.
 (b) Product obtained due to $\text{S}_{\text{N}}1$ reaction is a tertiary ether.
 (c) Product obtained due to $\text{S}_{\text{N}}2$ reaction is a primary ether.
 (d) None of these.

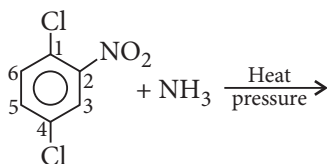
10. The major product formed in the reaction



SECTION - II

More than One Options Correct Type

11. Which of the following statements is false regarding following reaction?



- (a) No reaction is possible because $-\text{Cl}$ is present on benzene ring.
 (b) A nucleophilic substitution will take place in which both $-\text{Cl}$ will be replaced by two $-\text{NH}_2$ groups.

(c) A nucleophilic substitution will take place in which only $-\text{Cl}$ attached on C_1 will be replaced by $-\text{NH}_2$.

(d) A nucleophilic substitution will take place in which only $-\text{Cl}$ attached on C_4 will be replaced by $-\text{NH}_2$.

12. Reagent which cannot be used to distinguish allyl bromide from *n*-propyl bromide is/are

- (a) Br_2/CCl_4
 (b) shaking with an aqueous solution of AgNO_3
 (c) boiling with aqueous KOH solution followed by acidification with dil. HNO_3 and addition of AgNO_3 solution
 (d) fusion with Na followed by acidification with dilute HNO_3 and addition of AgNO_3 solution.

13. Which of the following methods cannot be used to prepare ethyl fluoride?

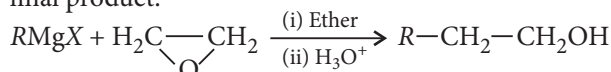
- (a) $\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{NaF/acetone}}$
 (b) $\text{CH}_3\text{CH}_3 \xrightarrow{\text{F}_2/h\nu}$
 (c) $\text{CH}_3\text{CH}_2\text{Cl} + \text{AgF} \longrightarrow$
 (d) $\text{CH}_2=\text{CH}_2 + \text{F}_2 \longrightarrow$

SECTION - III

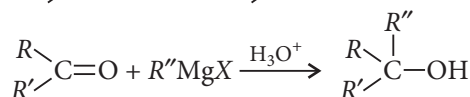
Paragraph Type

Paragraph for Questions 14 and 15

Grignard reagents are powerful nucleophiles and strong bases. They act as nucleophiles by attacking a variety of compounds including saturated and unsaturated carbon atoms. Examples of reaction on saturated carbon include oxiranes (epoxides) which form alcohols as the final product.



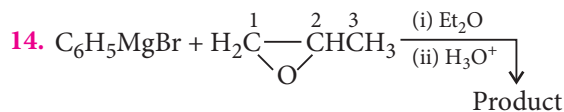
Examples of reaction on unsaturated carbon are attack on >C=O , $-\text{C}\equiv\text{N}$, $\text{>C}=\text{S}$ etc.



When R and $\text{R}' = \text{H}$, product is 1° alcohol.

When R and $\text{R}' = \text{Alkyl group}$, product is 3° alcohol.

When either R or R' is alkyl, and the second is H , product is 2° alcohol.



Here the nucleophile C_6H_5^- attacks on

- (a) C_1 (b) C_2
 (c) C_3 (d) any of the three.

15. Epoxides react with Grignard reagent to form
 (a) primary alcohols (b) secondary alcohols
 (c) tertiary alcohols (d) any of the three.

Paragraph for Questions 16 and 17

The majority of haloalkanes have a dipole moment. This is a result of the electron withdrawing ability of halogen atoms. The halogen atom carries a slight negative charge, with the remainder of the molecule having a slight positive charge. The carbon atom bonded to the halogen can act as a centre of attraction of nucleophiles. Atoms or molecules with lone pairs of electrons and/or a negative charge make good nucleophiles. However, equally important as far as a successful reaction is concerned is that the halogen atom makes a good leaving group. The majority of haloalkanes fit the same pattern in their reactions.

16. A solution of (+) 1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of SbCl_5 , due to the formation of
 (a) carbocation (b) carbanion
 (c) free radical (d) carbene.
17. The rate of $\text{S}_{\text{N}}2$ reaction is maximum when the solvent is
 (a) CH_3OH (b) H_2O
 (c) DMSO (d) benzene.

SECTION - IV

Matching List Type

18. Match the entries of List I with appropriate entries of List II and select the correct answer using the code given below the lists :

List I		List II		
P.	$\xrightarrow[\text{CuI}]{\text{Li}} \text{CH}_3\text{-CH}_2\text{-Cl}$	1.		
Q.	$\xrightarrow[\text{CuI}]{\text{Li}} \text{CH}_3\text{-CH}_2\text{-Br}$	2.		
R.	$\xrightarrow[\text{CuI}]{\text{Li}} \text{CH}_3\text{CH}_2\text{-Br}$	3.		
S.	$\xrightarrow[\text{CuI}]{\text{Li}} \text{CH}_3\text{CH}_2\text{-Br}$	4.		
	P Q R S			
(a)	1	2	3	4
(b)	4	3	1	2
(c)	3	4	2	1
(d)	2	1	4	3

19. Match the entries of List I with appropriate entries of List II and select the correct answer using the code given below the lists :

List I

(Reaction)

- P. $\text{CH}_3\text{-Br} \longrightarrow \text{CH}_3\text{-OH}$
 Q. $\text{CH}_3\text{-Cl} \longrightarrow \text{CH}_3\text{-OH}$
 R. $\text{CH}_3\text{-F} \longrightarrow \text{CH}_3\text{-OH}$
 S. $\text{CH}_3\text{-I} \longrightarrow \text{CH}_3\text{-OH}$

List II

(Relative rate)

1. 800
 2. 8000
 3. 6300
 4. 2700

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

SECTION - V

Assertion Reason Type

20. **Assertion :** Grignard reagents are prepared in ethers but not in benzene.
Reason : Grignard reagents are soluble in benzene.
21. **Assertion :** Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.
Reason : The reaction follows $\text{S}_{\text{N}}1$ mechanism.
22. **Assertion :** Chloral reacts with phenyl chloride to form DDT.
Reason : The reaction takes place in basic medium.

SECTION - VI

Integer Value Correct Type

23. The total number of alkenes possible by dehydrohalogenation of 3-bromo-3-cyclopentylhexane using alcoholic KOH is
24. An alkyl halide R-X gives nucleophilic substitution reaction with aqueous NaOH. The overall reaction rate in 0.01 M NaOH solution is given by the equation.
 $r = 2 \times 10^{-5} [\text{R-X}] [\text{OH}^-] + 3 \times 10^{-7} [\text{R-X}]$
 If the percentage yield of $\text{S}_{\text{N}}2$ reaction is represented as $(n \times 10)$ the value of n is
25. How many of the following alkyl halides would react by $\text{S}_{\text{N}}1$ mechanism?
 CH_3Br , $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$, $(\text{CH}_3)_3\text{C-Br}$,
 $\text{BrCH}_2\text{CH}=\text{CH}_2$, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, $(\text{CH}_3)_3\text{CCH}_2\text{Br}$,
 $\text{C}_6\text{H}_5\text{-CHBr-CH}_3$, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$

SOLUTIONS

SOLUTIONS

1. (c) : $x_A p_A^\circ + x_B p_B^\circ = p_{\text{total}}$
 $= \frac{1}{4} p_A^\circ + \frac{3}{4} p_B^\circ = 550 \text{ mm Hg}$... (i)

Again, $\frac{1}{5} p_A^\circ + \frac{4}{5} p_B^\circ = 560 \text{ mm Hg}$... (ii)

On solving equations (i) and (ii), we get $p_A^\circ = 400 \text{ mm Hg}$ and $p_B^\circ = 600 \text{ mm Hg}$

2. (a): Normality of oxalic acid solution

$$= \frac{6.3}{63} \times \frac{1000}{250} = 0.4 \text{ N}$$

Using normality equation, $N_1 V_1 = N_2 V_2$
 $0.1 \times V_1 = 0.4 \times 10 \Rightarrow V_1 = 40 \text{ mL}$

3. (d): Osmosis is the flow of the solvent (H_2O) molecules and not of ions. Hence, no colour change appears.

4. (c): For isotonic solutions, $\pi_1 = \pi_2$
 $\pi = CRT$

Then, $C_1 = C_2$ for isotonic solutions

$$C = \frac{n}{V}$$

Concentration of sucrose = $\frac{34.2}{342} = 0.1 \text{ M}$

Concentration of glucose = $0.1 = \frac{\text{Mass of glucose}}{180}$

\therefore Mass of glucose = 18 g/L
Hence, 18 g L^{-1} glucose is 0.1 M .

5. (c): ΔT_b for urea solution = $0.54 \text{ K} = K_b \times \text{molality} = K_b \times 1$

$\therefore K_b = 0.54 \text{ K kg mol}^{-1}$

$$\frac{\Delta p}{p^\circ} = \frac{w_2 M_1}{M_2 w_1} \Rightarrow \frac{w_2}{M_2 w_1} = \frac{\Delta p}{p^\circ M_1} = \frac{0.018}{18}$$

$$\Delta T_{b(\text{Glucose})} = \frac{1000 K_b w_2}{M_2 w_1} = 0.54 \text{ K}$$

6. (c): $p_A = p_A^\circ \times X_A = \text{Total pressure} \times Y_A$
 $p_B = p_B^\circ \times X_B = \text{Total pressure} \times Y_B$
Where X and Y represent mole fraction in liquid phase and vapour phase respectively.

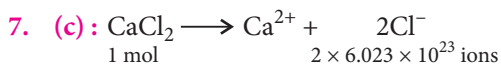
$\therefore \frac{p_B^\circ X_B}{p_A^\circ X_A} = \frac{Y_B}{Y_A}, \frac{p_B^\circ (1 - X_A)}{p_A^\circ X_A} = \frac{1 - Y_A}{Y_A}$

$$\frac{1}{X_A} - 1 = \frac{p_A^\circ}{p_B^\circ} \left(\frac{1}{Y_A} - 1 \right) = \frac{p_A^\circ}{p_B^\circ} \frac{1}{Y_A} - \frac{p_A^\circ}{p_B^\circ}$$

or,
$$\frac{1}{X_A} = \frac{p_A^\circ}{p_B^\circ} \cdot \frac{1}{Y_A} + \left(1 - \frac{p_A^\circ}{p_B^\circ} \right) = \frac{p_A^\circ}{p_B^\circ} \cdot \frac{1}{Y_A} + \frac{p_B^\circ - p_A^\circ}{p_B^\circ}$$

This is equation of straight line.

Slope = $\frac{p_A^\circ}{p_B^\circ}$, Intercept = $\frac{p_B^\circ - p_A^\circ}{p_B^\circ}$



$2 \times 6.023 \times 10^{23} \text{ Cl}^-$ ions are present in 1 mol CaCl_2
 $3.01 \times 10^{22} \text{ Cl}^-$ ions will be present in $\frac{1 \times 3.01 \times 10^{22}}{2 \times 6.02 \times 10^{23}} = 0.025 \text{ mol of CaCl}_2$

Molarity = $\frac{\text{Number of moles}}{\text{Volume of solution (in L)}}$

$$= \frac{0.025}{200} \times 1000 = 0.125 \text{ M}$$

8. (d): $p_{\text{Total}} = p_B^\circ X_B + p_T^\circ X_T$

$$= \frac{96.4 \times 5}{8.25} + \frac{28.9 \times 3.25}{8.25} = 69.8 \text{ torr}$$

9. (a): Let the atomic masses of A and B be a and b respectively. The molecular mass of AB_2 will be $(a + 2b) \text{ g mol}^{-1}$ and that of AB_4 will be $(a + 4b) \text{ g mol}^{-1}$
 $\Delta T_f = K_f m$

For AB_2 , $2.3 = \frac{5.1 \times 1 \times 1000}{(a + 2b) \times 20}$... (i)

For AB_4 , $1.3 = \frac{5.1 \times 1 \times 1000}{(a + 4b) \times 20}$... (ii)

On solving equations (i) and (ii),
 $a \approx 25$ and $b \approx 42$

10. (c): Lowering in weight of solution \propto solution pressure (p_s) and lowering in weight of solvent $\propto p^\circ - p_s$ ($\because p^\circ = \text{Vapour pressure of pure solvent}$)
Thus,
$$\frac{p^\circ - p_s}{p_s} = \frac{\text{Lowering in weight of solvent}}{\text{Lowering in weight of solution}} = \frac{0.05}{2.5}$$

But according to Raoult's law,

$$\frac{p^\circ - p_s}{p_s} = \frac{w_2}{M_2} \times \frac{M_1}{w_1} \therefore \frac{0.05}{2.5} = \frac{10 \times 18}{90 \times M_2}$$

$$\Rightarrow M_2 = \frac{10 \times 18 \times 2.5}{90 \times 0.05} = 100 \text{ g mol}^{-1}$$

11. (a,b,c): B.pt. of CCl_4 is lesser than that of SiCl_4 . The vapour must always be richer in more volatile component. Hence, the upper curve represents the composition of the vapour and the lower curve represents the composition of the solution at the corresponding b.pt.

12. (b,d)

13. (b,d): (b) and (d) show -ve deviations whereas (a) and (c) show +ve deviations.

14. (c): Total pressure, $p_T = p_A^\circ X_A + p_B^\circ X_B$

$$= p_A^\circ (1 - X_B) + p_B^\circ X_B \quad (\because X_A + X_B = 1)$$

$$= p_A^\circ - X_B (p_A^\circ - p_B^\circ)$$

Comparing with given equation, $p_A^\circ = 120$ torr
 $p_A^\circ - p_B^\circ = 75 \Rightarrow p_B^\circ = 45$ torr

15. (a): $p_T = 120 \times \frac{1}{3} + 45 \times \frac{2}{3} = 70$ torr
16. (d): In (a) and (b), the solutes undergo micellization in solution and in (c) the solute undergoes dimerisation. As a result, the observed colligative properties will be lower than the normal values.
17. (c): Normal value of $\Delta T_f = K_f m = 1.80 \times \frac{6}{60} = 0.18$ K
 Acetic acid is a uni-univalent weak electrolyte and ionises feebly, hence ' i ' is slightly greater than unity.
18. (c): P. All gases dissolve in water exothermically with decrease in randomness. Hence, $\Delta H < 0$ and $\Delta S < 0$.
 Q. Since solubility of the given solid in water increases on raising temperature, dissolution is endothermic. Hence, $\Delta H > 0$ and $\Delta S > 0$ (Increase in disorder on dissolution).
 R. In a saturated solution, there is no further dissolution of solid. Hence, $\Delta H = 0$ and $\Delta m = 0$.
 S. On adding solid to super saturated solution, excess of solid dissolved separated out with the evolution of heat. Hence, $\Delta H < 0$ and $\Delta m < 0$.

19. (b): 0.91% NaCl solution is isotonic with RBCs; $> 0.91\%$ is hypertonic; $< 0.91\%$ is hypotonic, 5.85% NaCl solution *i.e.*, 5.85 g NaCl in 100 mL solution means 1 N solution.
20. (a): This is according to Henry's law which states that the solubility of a gas in given volume of a liquid at a particular temperature is directly proportional to the pressure of gas above the liquid.
21. (b): One molar aqueous solution has 1 mole in less than 1000 g of water. Hence, 1000 g of water will be associated with more than 1 mole while 1 molal has 1 mole in 1000 g of water.
22. (b): Non-ideal solutions show positive or negative deviations.
23. (3): $\alpha = \frac{i-1}{n-1} \Rightarrow 0.5 = \frac{i-1}{5-1} \Rightarrow i = 3$
24. (3): Coolant is glycol ($C_2H_6O_2$) and is non-electrolyte.

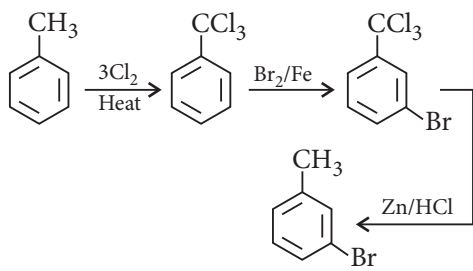
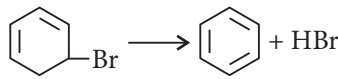
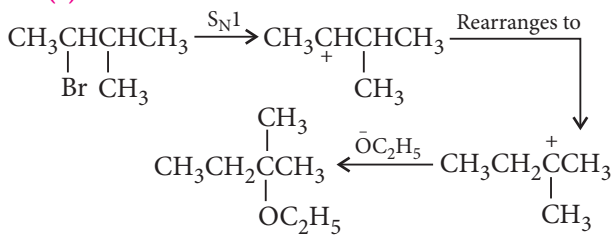
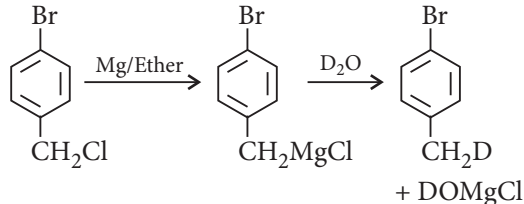
$$\Delta T_f = 2.8^\circ = \frac{1000 K_f w_2}{M_2 w_1}, 2.8 = \frac{1000 \times 1.86 \times w_2}{62 \times 1000}$$

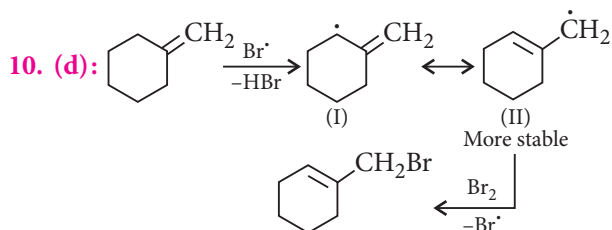
$$\therefore w_2 \approx 93 \text{ g} = (90 + 3) \text{ g} \Rightarrow x = 3$$

25. (8): Stock solution of HCl = 29.2% (w/w) *i.e.*, 29.2 g of HCl are present in 100 g of the solution. As density of solution = 1.25 g mL^{-1} , volume of 100 g of solution = $\frac{100}{1.25} \text{ mL}$. As molecular weight of HCl is 36.5 g mol^{-1} , molarity of the solution = $\frac{29.2}{36.5} \times \frac{1.25}{100} \times 1000 = 10 \text{ M}$

$$M_1 V_1 = M_2 V_2$$
 (Stock solution) (Solution required)
 $10 \times V_1 = 0.4 \times 200 \Rightarrow V_1 = 8 \text{ mL}$

HALOALKANES AND HALOARENES

1. (b): 
2. (a): It is Wurtz reaction, both alkyl halide being aliphatic.
3. (b) 4. (c)
5. (c): 
- It results in formation of more stable aromatic compound which is benzene.
6. (c): 
7. (c): 
8. (a): $CH_3CH_2CH_2Br \xrightarrow{\text{Aq. NaOH}} CH_3CH_2CH_2OH$
 $CH_3CH_2CH_2Br \xrightarrow{Cl_2/H_2O} CH_3CH=CH_2 \xrightarrow[-H_2O]{Al_2O_3, \Delta} CH_3-CHOH-CH_2Cl$
9. (a): There is no chiral carbon, hence inversion does not take place.



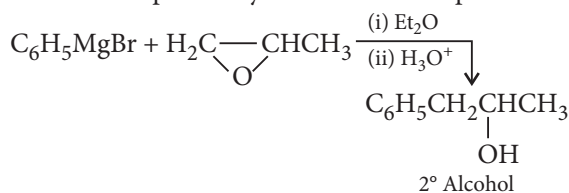
Free radical (II) is formed because endocyclic double bond is more stable than exocyclic double bond.

11. (a,b,d): $-\text{Cl}$ group present in the o - and p -positions to the electron-withdrawing group is activated towards nucleophilic substitution, hence only $-\text{Cl}$ present on the o - and/or p -position to the $-\text{NO}_2$ group will be replaced.

12. (c,d): Br_2/CCl_4 can be used, allyl bromide being unsaturated will discharge its colour while n -propyl bromide does not. On shaking with aq. AgNO_3 , allyl bromide being more reactive will give pale yellow ppt. of AgBr but n -propyl bromide will not. On boiling with aq. KOH , both will undergo hydrolysis, hence give ppt. of AgBr . Fusion with sodium also converts the bromine of both the compounds into NaBr , thus both give ppt. with AgNO_3 . Hence, reagents given in option (c) and (d) cannot be used to distinguish between allyl bromide and n -propyl bromide.

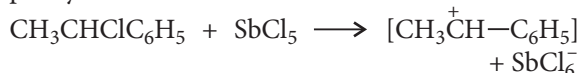
13. (a,b,d)

14. (a): Grignard reagents react primarily at the less substituted ring carbon atom of substituted oxiranes because comparatively it is more electrophilic.



15. (d): Depending on the type of oxirane 1°, 2° and 3° alcohols are formed when oxiranes react with Grignard reagents.

16. (a): In the presence of SbCl_5 , 1-chloro-1-phenylethane forms a carbocation as follows :



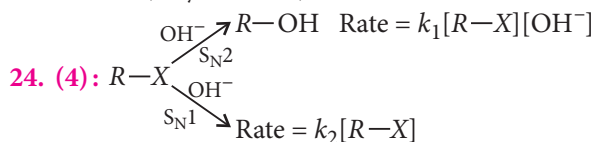
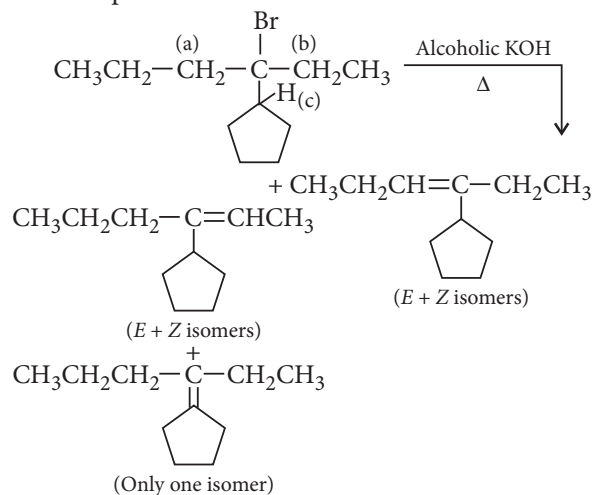
17. (c): Polar aprotic solvents such as DMSO increase the rate of the $\text{S}_{\text{N}}2$ reactions.

18. (d) 19. (a)

20. (c): Grignard reagents are soluble in ether but not in benzene.

21. (a) 22. (c)

23. (5): 3-Bromo-3-cyclopentylhexane has three different types of β -hydrogens marked as (a), (b) and (c) and hence can give three structurally isomeric alkenes. But two of these can exhibit geometrical isomerism. Therefore, total number of alkenes possible are five as shown below :



24. (4): Overall reaction rate = $k_1[\text{R}-\text{X}] + k_2[\text{R}-\text{X}][\text{OH}^-]$
For 0.01 M NaOH solution

$$r = \underbrace{2 \times 10^{-5}[\text{R}-\text{X}](0.01)}_{\text{S}_{\text{N}}2} + \underbrace{3 \times 10^{-7}[\text{R}-\text{X}]}_{\text{S}_{\text{N}}1}$$

$$r = 2 \times 10^{-7}[\text{R}-\text{X}] + 3 \times 10^{-7}[\text{R}-\text{X}]$$

$$\% \text{ of } \text{S}_{\text{N}}2 \text{ reaction} = \frac{2 \times 10^{-7}}{2 \times 10^{-7} + 3 \times 10^{-7}} \times 100$$

$$= \frac{2}{5} \times 100 = 40 = 4 \times 10$$

25. (6): Alkyl halides that can form 3°, allylic or benzylic carbocations react by $\text{S}_{\text{N}}1$ mechanism. These are $(\text{CH}_3)_3\text{CBr}$, $\text{BrCH}_2\text{CH}=\text{CH}_2$, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, $(\text{CH}_3)_3\text{CCH}_2\text{Br}$, $\text{C}_6\text{H}_5\text{CHBrCH}_3$ and $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$.

MPP-2 CLASS XI

ANSWER KEY

1. (b)	2. (b)	3. (d)	4. (c)	5. (a)
6. (b)	7. (d)	8. (b)	9. (d)	10. (d)
11. (d)	12. (c)	13. (a)	14. (d)	15. (a)
16. (c)	17. (d)	18. (c)	19. (a)	20. (a,c)
21. (a,b,c)	22. (a,b,c,d)	23. (a,c,d)	24. (2)	25. (4)
26. (2)	27. (b)	28. (b)	29. (c)	30. (a)

CLASS XII Series 3

ACE YOUR WAY

CBSE



General Principles and Processes of Isolation of Elements | *p*-Block Elements

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

- All questions are compulsory.
- Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- Q. no. 23 is a value based question and carries 4 marks.
- Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- Use log tables if necessary, use of calculators is not allowed.

	Previous Years Analysis					
	2016		2015		2014	
	Delhi	AI	Delhi	AI	Delhi	AI
VSA	1	1	1	–	1	2
SA-I	–	1	–	1	2	3
SA-II	1	2	1	2	2	1
VBQ	–	–	–	–	–	–
LA	1	–	1	–	1	–

- Why is limestone added to the ore in the extraction of iron in blast furnace?
- Account for the following :
BiH₃ is the strongest reducing agent amongst all the hydrides of group 15.
- Why the compounds of fluorine with oxygen are called fluorides of oxygen and not the oxides of fluorine?
- Which of the following ores can be concentrated by froth floatation method and why?
Fe₂O₃, ZnS, Al₂O₃
- Why is HF weakest acid among hydrohalic acid?
- Why is copper matte put in silica lined converter?
- (i) Which noble gas is used in filling balloons for meteorological observations?
(ii) Complete the following reaction :
 $\text{XeF}_2 + \text{PF}_5 \longrightarrow$
- The value of $\Delta_f G^\circ$ for the formation of Cr₂O₃ is – 540 kJ mol⁻¹ and that of Al₂O₃ is – 827 kJ mol⁻¹. Is the reduction of Cr₂O₃ possible with Al?

OR

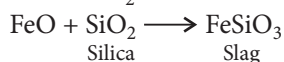
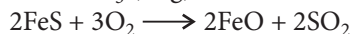
- The extraction of gold by leaching with NaCN involves both oxidation and reduction. Justify giving chemical equations.
- Why is SO₂ a better reducing agent in alkaline medium as compared to that in the acidic medium?
 - Arrange the following in the order of property indicated for each set.
 - F₂, Cl₂, Br₂, I₂ (increasing bond dissociation enthalpy)
 - HOCl, HOBr, HOI (increasing acid strength)
 - (i) Graphite can be used as an anode but not diamond. Why?
(ii) How will you separate Ni from CO?
 - Draw the following structures :
 - H₂SO₃
 - H₂SO₄
 - H₂S₂O₇
 - (i) What happens when PCl₅ is heated?
(ii) How is O₃ estimated quantitatively?
(iii) What is the basicity of H₃PO₄?

14. What are the chief ores of zinc? Write chemical reactions taking place in the extraction of zinc from zinc blende.
15. Give reasons :
- Nitrogen cannot expand its covalency beyond 4.
 - Sulphurous acid acts as a reducing agent.
 - HF is not stored in glass bottles.
16. (i) Out of C and CO which is a better reducing agent for ZnO?
 (ii) Why is the reduction of a metal oxide easier if the metal is formed in liquid state at the temperature of reduction?
17. Answer the following :
- How PH_3 is basic in nature? Explain.
 - Complete the following reactions :
 - $\text{NaOH} + \text{Cl}_2 \xrightarrow{\text{hot and conc.}}$
 - $\text{NH}_3 + \text{Cl}_2 \xrightarrow{\text{excess}}$
- OR**
- Explain why in spite of nearly same electronegativity, oxygen forms hydrogen bonding while chlorine does not.
 - Out of noble gases, only xenon is known to form chemical compounds.
 - IF_7 exists but BrF_7 does not exist. Why?
18. (i) Why is aluminium a good reducing agent?
 (ii) Which method would you suggest for the separation of the metals in the following mixtures?
 (a) Zinc and iron (b) Copper and magnesium
 Give reason for your choice.
19. Answer the following :
- NCl_3 gets hydrolysed while NF_3 does not. Why?
 - Write the structural difference between white P and red P.
 - Write the product formed when concentrated H_2SO_4 is added to calcium fluoride.
20. (i) Why are group 16 elements called chalcogens?
 (ii) Give reason for the following :
 (a) Fluorine exhibits only - 1 oxidation state.
 (b) Fluorine is the strongest oxidising agent.
21. (i) Although carbon and hydrogen are better reducing agents but they are not used to reduce metallic oxides at high temperature. Why?
 (ii) Which method is used for refining Zr and Ti? Explain with equation.
22. Give reasons for the following :
- CN^- ion is known but CP^- ion is not known.
 - NO_2 dimerises to form N_2O_4 .
 - ICl is more reactive than I_2 .
23. Aashish, a class XII student was adding water to conc. H_2SO_4 but he was stopped by Aashmi, a fellow student who explained Aashish that always acid is added to water dropwise with constant stirring not vice versa otherwise it will lead to spurting out of acid from the test tube. Answer the following :
- Why always acid is added to water?
 - What values are shown by Aashmi?
 - Which process is used to prepare sulphuric acid?
 - Give molecular formulae of hydrate of H_2SO_4 .
24. A translucent white waxy solid (A) on heating in an inert atmosphere is converted into its allotropic form (B). Allotrope (A) on reaction with very dilute aqueous KOH liberates a highly poisonous gas (C) having rotten fish smell. With excess of chlorine, (C) forms (D) which hydrolyses to a compound (E). Identify (A) to (E).
- OR**
- An amorphous solid 'A' burns in air to form a gas 'B' which turns lime water milky. The gas is also produced as a by-product during roasting of sulphide ore. This gas decolourises acidified aqueous KMnO_4 solution and reduces Fe^{3+} to Fe^{2+} . Identify the solid A and the gas B and write the reactions involved.
25. (i) Free energies of formation ($\Delta_f G$) of $\text{MgO}_{(s)}$ and $\text{CO}_{(g)}$ at 1273 K and 2273 K are given below :
- $$\Delta_f G(\text{MgO})_{(s)} = -941 \text{ kJ mol}^{-1} \text{ at } 1273 \text{ K}$$
- $$\Delta_f G(\text{MgO})_{(s)} = -314 \text{ kJ mol}^{-1} \text{ at } 2273 \text{ K}$$
- $$\Delta_f G(\text{CO})_{(g)} = -439 \text{ kJ mol}^{-1} \text{ at } 1273 \text{ K}$$
- $$\Delta_f G(\text{CO})_{(g)} = -628 \text{ kJ mol}^{-1} \text{ at } 2273 \text{ K}$$
- On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for $\text{MgO}_{(s)}$.
- Name an ore having two different metal ions.
 - Why zinc and not copper is used for the recovery of Ag from $[\text{Ag}(\text{CN})_2]^-$?
- OR**
- Name the metals which are associated with the following terms in their extraction from their ores :
 (a) Bessemer's converter (b) Blast furnace
 (c) Alumino thermic process
 (d) Magnetic separation
 - What criterion is followed for the selection of the stationary phase in chromatography?
 - Explain the method used for the purification of germanium.

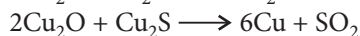
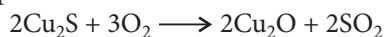
26. (i) (a) Does the hydrolysis of XeF_6 lead to a redox reaction?
 (b) Draw the structure of XeOF_4 .
 (c) Complete and balance the following equation :
 $\text{XeF}_4 + \text{H}_2\text{O} \longrightarrow$
- (ii) Account for the following :
 (a) H_2S has lower boiling point than H_2O .
 (b) Reducing character decreases from SO_2 to TeO_2 .
- OR**
- (i) How would you account for the following?
 (a) Fluorine atom is more electronegative than iodine atom, yet HF is weaker acid than HI .
 (b) Cl has more electron gain enthalpy than F .
- (ii) Give the structure of PCl_5 in
 (a) the vapour phase (b) the solid state.
- (iii) Why does a nitric acid bottle appear yellow?

SOLUTIONS

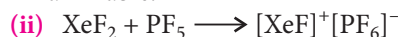
- Limestone is added to remove impurity of silica as fusible slag.
 $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$; $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$
- Among hydrides of group-15 elements, the bond length increases from N-H to Bi-H with increase in size of elements. Bi-H bond is longest and weakest, it can break more easily and evolve H_2 gas. Thus, BiH_3 is the strongest reducing agent.
- Fluorine is more electronegative than oxygen, thus, electrons are more towards fluorine than oxygen atom. Hence, they exist as fluorides of oxygen.
- Froth floatation method is used to remove gangue from sulphide ores. Thus, ZnS can be concentrated by froth floatation method.
- HF has high bond dissociation enthalpy than other hydrohalic acid which leads to lower degree of ionisation of HF . Thus, HF is the weakest acid.
- Copper matte consists of Cu_2S and FeS . When a blast of hot air is passed through molten matte taken in a silica lined converter, FeS present in matte is oxidised to FeO which combines with silica (SiO_2) to form FeSiO_3 (slag).



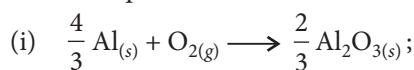
When complete iron has been removed as slag, some of the Cu_2S undergoes oxidation to form Cu_2O which then reacts with more Cu_2S to form copper metal.



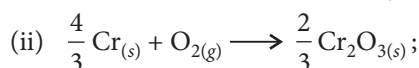
7. (i) Helium is used for filling balloons for meteorological observations because it is non-inflammable.



8. The two equations are :

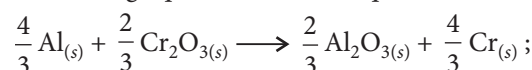


$$\Delta_f G^\circ_{\text{Al, Al}_2\text{O}_3} = -827 \text{ kJ mol}^{-1}$$



$$\Delta_f G^\circ = -540 \text{ kJ mol}^{-1}$$

Subtracting equation (ii) from equation (i), we get

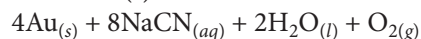


$$\Delta_r G^\circ = -287 \text{ kJ mol}^{-1}$$

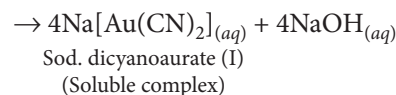
Since $\Delta_r G^\circ$ is negative, thus, reduction of Cr_2O_3 by Al is possible.

OR

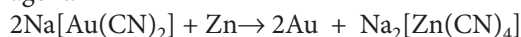
During the leaching process, Au is first oxidised to Au^+ by O_2 of the air which then combines with CN^- ions to form the soluble complex, sodium dicyanoaurate (I).



Gold (Impure)



Gold is then extracted from this complex, by displacement method using a more electropositive zinc metal. In this reaction, Zn acts as a reducing agent.



Gold Sod. tetracyanozincate (II)

Thus, extraction of Au by leaching with NaCN involves both oxidation and reduction.

9. SO_2 acts as a reducing agent in aqueous solution because of the following reaction :



Nascent hydrogen

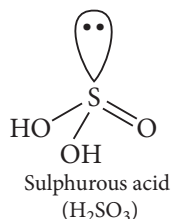
In alkaline medium, the OH^- will combine with H^+ from H_2SO_4 and will be removed as weakly ionisable H_2O . This will shift the reaction in the forward direction and, therefore, SO_2 will act as a better reducing agent in alkaline medium.

10. (i) $\text{I}_2 < \text{F}_2 < \text{Br}_2 < \text{Cl}_2$ (increasing bond dissociation enthalpy).
 (ii) $\text{HOCl} > \text{HOBr} > \text{HOI}$ (increasing acid strength).
11. (i) Graphite is a good conductor of electricity due to the presence of free electrons within its layers

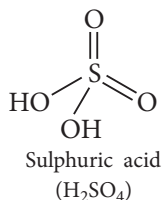
whereas diamond is a bad conductor of electricity due to the absence of free electrons in its structure. Therefore, diamond cannot be used as anode.

(ii) When impure Ni is heated in a current of CO at temperature 330-350 K, Ni forms volatile Ni(CO)₄. The volatile Ni(CO)₄ is separated. It is then heated at 450-470 K to get pure Ni.

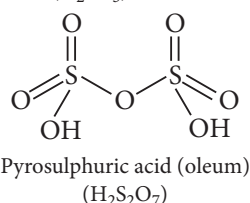
12. (i)



(ii)



(iii)



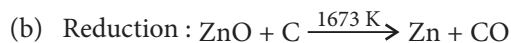
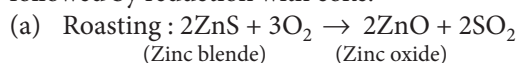
13. (i) On heating, PCl₅ sublimes but decomposes to PCl₃ and Cl₂ on stronger heating.

(ii) When ozone reacts with an excess of KI solution buffered with a borate buffer (pH = 9.2), iodine is liberated which can be titrated against standard solution of sodium thiosulphate. This is used as a method of estimation of ozone quantitatively.

(iii) Three P—OH groups are present in the molecule of H₃PO₄. Therefore, its basicity is three.

14. The chief ores of zinc are zinc blende (ZnS), calamine (ZnCO₃), zincite (ZnO).

From zinc blende, zinc is extracted by roasting followed by reduction with coke.



The metal is distilled off and collected by rapid chilling.

15. (i) Nitrogen does not have vacant *d*-orbital to accommodate unpaired *s*-electron. Thus, it can have maximum covalency of 4 by using one *s*-orbital and three *p*-orbitals.

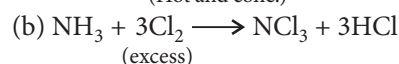
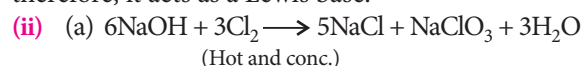
(ii) Sulphurous acid can easily be oxidized to sulphuric acid due to the presence of a lone pair of electrons on the sulphur atom. Hence, it acts as a strong reducing agent.

(iii) HF attacks glass by reacting with silicates of sodium and calcium in glass to form complex fluorides so, it is not stored in glass.

16. (i) Carbon is a better reducing agent for ZnO :
 $\text{ZnO} + \text{C} \xrightarrow{1673\text{ K}} \text{Zn} + \text{CO}$

(ii) Entropy change, Δ*S* of the reduction process is more positive when the metal formed is in liquid state and metal oxide being reduced is in the solid state. Since the value of *T*Δ*S* increases and that of Δ*H* remains constant, therefore, according to the equation Δ*G* = Δ*H* – *T*Δ*S* the value of Δ*G* becomes more negative and therefore, reaction becomes easier.

17. (i) PH₃ reacts with acids like HI to form phosphonium iodide which shows that PH₃ is basic in nature. This basic nature of PH₃ is due to the presence of lone pair on phosphorus atom and therefore, it acts as a Lewis base.



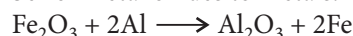
OR

(i) Oxygen has smaller size than chlorine. The smaller size of oxygen favours hydrogen bonding. In other words, though electronegativity of Cl is same as that of O, it does not form hydrogen bonding because of its larger size.

(ii) Except radon, which is radioactive, xenon has lowest ionisation enthalpy among noble gases and hence it readily forms chemical compounds particularly, with O₂ and F₂.

(iii) The atomic size of iodine (133 pm) is much bigger than bromine (114 pm). Therefore, seven small sized F atoms can be accommodated around big I atom but not around small sized Br atom.

18. (i) Aluminium has more affinity for oxygen and is thus readily oxidised. Therefore, it reduces a large number of metal oxides to metals.



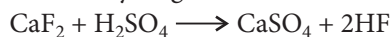
(ii) (a) Zinc and iron can be separated by using distillation. Zn being a low boiling metal will distill out first leaving behind iron.

(b) Copper and magnesium can be separated by using electrolytic reduction. Copper being below hydrogen in the activity series of metal is produced first at the cathode leaving behind magnesium in the solution.

19. (i) In NCl₃, Cl has vacant *d*-orbitals to accept lone pair of electrons present on oxygen atom of water molecule while no such vacant orbital is available on F atom in NF₃.

(ii) White P consists of P_4 units in which four P atoms lie at the corners of a regular tetrahedron with $\angle PPP = 60^\circ$. Red P also consists of P_4 tetrahedra units but it has polymeric structure consisting of P_4 tetrahedra linked together by covalent bonds.

(iii) It forms hydrogen fluoride :



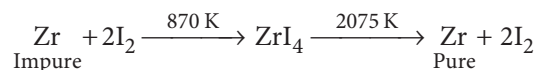
20. (i) Chalcogens means ore forming. As most of the ores in the earth crust are either oxides or sulphides, thus, group 16 elements are called chalcogens.

(ii) (a) Fluorine is short of only one electron to complete its octet. Due to high electronegativity and non-availability of d -atomic orbitals, it shows only -1 oxidation state.

(b) F_2 is the strongest oxidising agent due to low $F-F$ bond enthalpy and very high hydration energy of F^- .

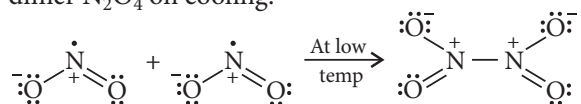
21. (i) This is because at high temperature carbon and hydrogen react with metals to form carbides and hydrides respectively.

(ii) van Arkel method is used for refining Zr and Ti. In this method crude metal is heated with iodine in an evacuated vessel to form volatile unstable compound. The compound is then decomposes to get pure metal.



22. (i) Due to smaller size and higher electronegativity than phosphorus, N is able to form $p\pi-p\pi$ multiple bonds with C and hence, forms $:\text{C}\equiv\text{N}:$ ion but due to bigger size and lower electronegativity, P is not able to form multiple bonds with C and hence, does not form $:\text{C}\equiv\text{P}:$ ion.

(ii) NO_2 is an odd electron species ($7 + 8 + 8 = 23$ electrons), with odd electrons present on N and therefore, in order to get more stability, the two odd electrons pair up to form the dimer N_2O_4 on cooling.



(iii) As $I-Cl$ bond is weaker as compared to $I-I$ bonds in I_2 , ICl is more reactive than I_2 .

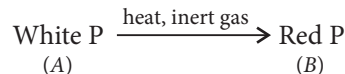
23. (i) Strong acids like sulphuric acid has strong affinity for water and the dissolution process in highly exothermic. Thus, acid is added to water slowly, so that heat evolved is absorbed by water and spurting does not occur.

(ii) Good knowledge of concepts and concern towards fellow students.

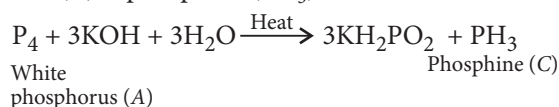
(iii) Contact process.

(iv) $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$

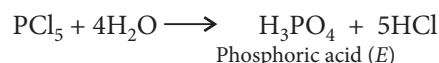
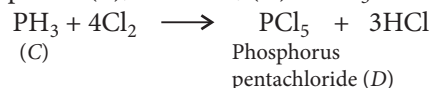
24. As the white waxy solid (A) on heating in an inert atmosphere, is converted into its allotrope (B), therefore, solid (A) must be white phosphorus.



As (A) on heating with dilute solution of KOH gives a highly poisonous gas (C) having the smell of rotten fish, it confirms that (A) is white phosphorus and (C) is phosphine (PH_3).

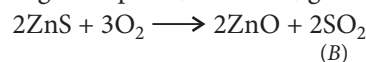


Phosphine (C) reacts with excess of Cl_2 to form a compound (D) which on hydrolysis gives compound (E), therefore, (D) is PCl_5 .

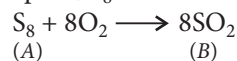


OR

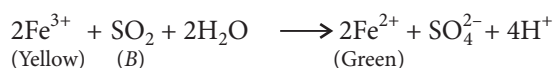
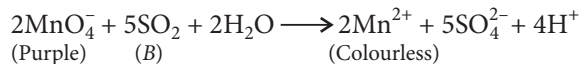
Since gas 'B' is obtained as a by-product during roasting of sulphide, therefore, gas 'B' must be SO_2 .



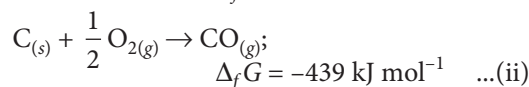
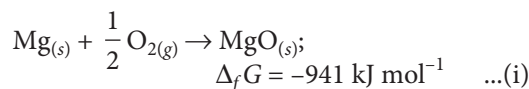
Since gas 'B' is obtained when amorphous solid 'A' burns in air, therefore, amorphous solid 'A' must be sulphur, S_8 .



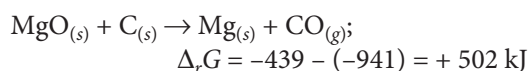
Gas 'B' reduces acidified KMnO_4 solution and reduces Fe^{3+} to Fe^{2+} salts as shown below :



25. (i) At 1273 K,

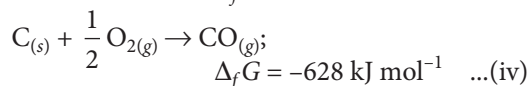
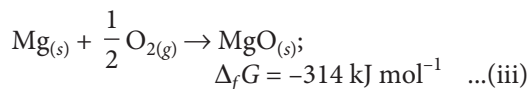


Redox reaction for reduction of MgO by C can be obtained by subtracting eqn (i) from eqn (ii).

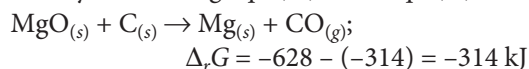


As, $\Delta_r G$ is +ve, reaction is not feasible.

At 2273 K,



The redox reaction for reduction of MgO by C is obtained by subtracting eqn (iii) from eqn (iv).



As $\Delta_r G$ for the reaction is -ve, the reaction is feasible. Therefore, $\text{C}_{(s)}$ will reduce MgO to Mg.

(ii) Dolomite, is $\text{MgCO}_3 \cdot \text{CaCO}_3$.

(iii) E° of Zn ($E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76$) is lower than that of copper ($E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34$), therefore, Zn is a stronger reducing agent than Cu. Thus, zinc reduces $[\text{Ag}(\text{CN})_2]^-$ to metallic Ag.

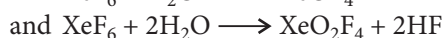
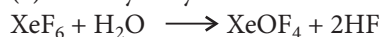
OR

- (i) (a) Copper (b) Iron
 (c) Iron, chromium, manganese
 (d) Tin, iron, manganese

(ii) The stationary phase is selected in such a way that the impurities are more strongly adsorbed on the stationary phase than element to be purified. Under these conditions when the column is extracted, the impurities will be retained by the stationary phase while pure component is easily eluted.

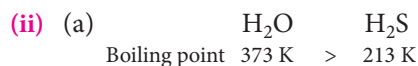
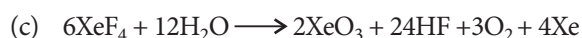
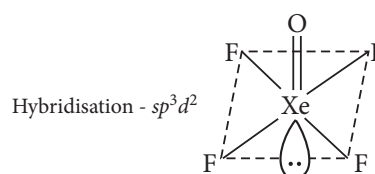
(iii) Zone refining is used for the purification of germanium. In this process, an impure metal rod is taken and heated at one end so that this end melts and forms molten zone. By slowly moving the heat source along the length of the rod the pure metal crystallises out of the melt whereas the impurities pass into the adjacent molten zone. This process is repeated several times till the impurities are completely driven to one end of the rod which is then cut off and discarded.

26. (i) (a) The hydrolysis reaction of XeF_6 is



The oxidation states of all the elements remain the same hence, it is not a redox reaction.

(b) XeOF_4 is square pyramidal.



The abnormally high boiling point of H_2O is due to strong intermolecular H-bonding. Since, all other elements have much lower electronegativity than oxygen, they do not undergo H-bonding.

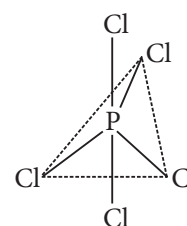
(b) The +6 oxidation state of S is more stable than +4 therefore, SO_2 acts as a reducing agent. Further, since the stability of +6 oxidation decreases from S to Te therefore, the reducing character of the dioxides decreases from SO_2 to TeO_2 .

OR

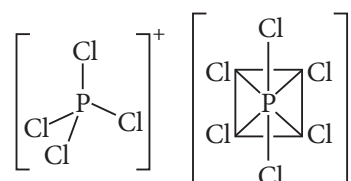
(i) (a) Fluorine atom is smaller in size than iodine atom and therefore, bond dissociation enthalpy of H—F is very high than the H—I bond. Hence, HI is a stronger acid than HF.

(b) F is very small in size so the electron density is very high. The addition of an extra electron results in more electron-electron repulsion. Hence, the electron gain enthalpy of F is less than that of chlorine.

(ii) (a) In vapour phase, PCl_5 has a trigonal bipyramidal structure.



(b) In solid state, PCl_5 exists as $[\text{PCl}_4]^+ [\text{PCl}_6]^-$ and the structure is



(iii) The yellow colour of the concentrated nitric acid bottle is due to the partial decomposition of the HNO_3 to nitrogen dioxide.



MPP-2 MONTHLY Practice Problems

Class XII

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Solutions | Electrochemistry

Total Marks : 120

Time Taken : 60 Min.

NEET / AIIMS

Only One Option Correct Type

- 5 cm³ of acetone is added to 100 cm³ of water. The vapour pressure of water over the solution
 - will be equal to the vapour pressure of pure water
 - will be less than the vapour pressure of pure water
 - will be greater than the vapour pressure of pure water
 - will be very large.
- What is the E_{cell} of the given cell?
 $\text{Zn} | \text{Zn}^{2+} (2 \text{ M}) || \text{Zn}^{2+} (10 \text{ M}) | \text{Zn}$
 - Zero
 - 0.0206 V
 - 5.00 V
 - Data is insufficient
- The decrease in the freezing point of an aqueous solution of a substance is 1.395 K and, the decrease in the freezing point of a benzene solution of the same substance is 1.280 K. The difference in ΔT is due to the reason that
 - the substance dissociates in the aqueous solution as well as in the benzene solution
 - the substance associates in the benzene solution
 - the substance dissociates in the aqueous solution and not in the benzene solution
 - the substance forms complexes in solution.
- The vapour pressure of pure liquid solvent *A* is 0.80 atm. When a non-volatile substance *B* is added to the solvent, its vapour pressure drops to 0.60 atm. Mole fraction of the component *B* in the solution is
 - 0.50
 - 0.25
 - 0.75
 - 0.40
- When a crystal of the solute is introduced into a super saturated solution of the solute
 - the solute dissolves
 - the excess solute crystallizes out
 - the solution becomes unsaturated
 - the solution remains super saturated.
- In $\text{H}_2\text{-O}_2$ fuel cell, which of the following is correct when an alkali is used as electrolyte?
 - At anode : $\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \longrightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-$
 - At cathode : $\text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{OH}^-(\text{aq})$
 - Net reaction : $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$
 - All of these
- The dissolving process is exothermic when
 - the energy released in solvation exceeds the energy used in breaking up solute-solute and solvent-solvent interactions
 - the energy used in solvation exceeds the energy released in breaking up solute-solute and solvent-solvent interactions
 - the energy released in solvation is about the same as the energy used in breaking up solute-solute and solvent-solvent interactions
 - the energy used in solvation is about the same as the energy used in breaking up solute-solute and solvent-solvent interactions.
- KCl, BaCl₂ and AlCl₃ are used as electrolytes in three different cells connected in series. If 3 F charge is passed, the molar ratio of masses of K, Ba and Al deposited at cathodes will be
 - 1 : 1 : 1
 - 1 : 2 : 3
 - 3 : 2 : 1
 - none of these.
- The ionic mobility of alkali metal ions in aqueous solution is maximum for
 - K⁺
 - Rb⁺
 - Li⁺
 - Na⁺
- The standard e.m.f. of a cell, involving one electron change is found to be 0.591 at 25°C. The equilibrium constant of the reaction is ($F = 96500 \text{ C mol}^{-1}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

- (a) 1.0×10^1 (b) 1.0×10^{30}
 (c) 1.0×10^{10} (d) 1.0×10^5

11. An aqueous solution of a solute AB has boiling point of 101.08°C (AB is 100% ionised at boiling point of the solution) and freezes at -1.80°C . ($K_b/K_f = 0.3$) Hence, AB
 (a) is 100% ionised at the freezing point of the solution
 (b) behaves as non-electrolyte at the freezing point of the solution
 (c) forms dimer (d) none of these.
12. In a cell that utilises the reaction :
 $\text{Zn}_{(s)} + 2\text{H}^+_{(aq)} \longrightarrow \text{Zn}^{2+}_{(aq)} + \text{H}_{2(g)}$, addition of H_2SO_4 to cathode compartment will
 (a) increase the E and shift equilibrium to the left
 (b) lower the E and shift equilibrium to the right
 (c) increase the E and shift equilibrium to the right
 (d) lower the E and shift equilibrium to the left.

Assertion & Reason Type

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

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

13. **Assertion :** The freezing point of water is depressed by the addition of glucose.

Reason : Entropy of solution is less than entropy of pure solvent.

14. **Assertion :** Addition of HgI_2 to $\text{KI}_{(aq)}$ shows an increase in vapour pressure of solvent.

Reason : Addition of HgI_2 to KI causes increase in effective number of particles.

15. **Assertion :** In electrolysis, the quantity of electricity needed for depositing 1 mole of silver is different from that required for 1 mole of copper.

Reason : The molecular weights of silver and copper are different.

JEE MAIN / JEE ADVANCED / PETS

Only One Option Correct Type

16. Two liquids X and Y are perfectly immiscible. If X and Y have molecular masses in ratio 1 : 2, the total vapour pressure of a mixture of X and Y prepared in weight ratio 2 : 3 should be ($P_X^\circ = 400$ torr, $P_Y^\circ = 200$ torr)

- (a) 300 torr (b) 466.7 torr
 (c) 600 torr (d) 700 torr

17. A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode are respectively

- (a) O_2, H_2 (b) $\text{S}_2\text{O}_8^{2-}, \text{Na}$
 (c) O_2, Na (d) $\text{S}_2\text{O}_8^{2-}, \text{H}_2$

18. From the following E° values of half cells

- (i) $\text{A} + \text{e}^- \longrightarrow \text{A}^-; E^\circ = -0.24$ V
 (ii) $\text{B}^- + \text{e}^- \longrightarrow \text{B}^{2-}; E^\circ = +1.25$ V
 (iii) $\text{C}^- + 2\text{e}^- \longrightarrow \text{C}^{3-}; E^\circ = -1.25$ V
 (iv) $\text{D} + 2\text{e}^- \longrightarrow \text{D}^{2-}; E^\circ = +0.68$ V

What combination of two half cells would result in a cell with the largest potential?

- (a) (ii) and (iii) (b) (ii) and (iv)
 (c) (i) and (iii) (d) (i) and (iv)

19. At 12°C , the osmotic pressure of a urea solution is 500 mm Hg. When the solution is diluted and the temperature is raised to 27°C , the osmotic pressure is found to be 100 mm. The extent of dilution is

- (a) 2.3 (b) 5.0
 (c) 5.3 (d) cannot be calculated.

More than One Options Correct Type

20. Which of the following statements are correct?

- (a) Critical solution temperature is that temperature above or below which the two partially miscible liquids are completely soluble.
 (b) Phenol-water has both upper critical solution temperature and also lower critical solution temperature.
 (c) Phenol-water has only upper critical solution temperature.
 (d) Nicotine and water has both upper and lower critical solution temperature.

21. Select the correct statements if 9.65 ampere current is passed for 1 hour through the cell

- $\text{Ag} | \text{Ag}^+_{1\text{M}} || \text{Cu}^{2+}_{1\text{M}} | \text{Cu}$
 (a) Ag will get oxidised to Ag^+ and new $[\text{Ag}^+] = 1.36$ M
 (b) Ag^+ will get reduced to Ag and new $[\text{Ag}^+] = 0.64$ M
 (c) Cu^{2+} will get reduced to Cu and new $[\text{Cu}^{2+}] = 0.82$ M
 (d) Cu will get oxidised to Cu^{2+} and new $[\text{Cu}^{2+}] = 0.82$ M

22. Which of the following statements is/are correct?

- (a) The conductance of one cm^3 (or 1 unit^3) of a solution is called specific conductance.

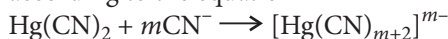
- (b) Specific conductance increases while molar conductivity decreases on progressive dilution.
 (c) The limiting equivalent conductivity of weak electrolyte cannot be determined exactly by extrapolation of the plot of Λ_{eq} against \sqrt{c} .
 (d) The conductance of metals is due to the movement of free electrons.

23. Which of the following combinations are correct for a binary solution in which the solute as well as the solvent are liquids?

- (a) C_6H_6 and $C_6H_5CH_3$; $\Delta H_{soln} > 0$; $\Delta V_{sol} = 0$
 (b) CH_3COCH_3 and $CHCl_3$; $\Delta H_{soln} < 0$; $\Delta V_{sol} < 0$
 (c) H_2O and HCl ; $\Delta H_{soln} > 0$; $\Delta V_{sol} < 0$
 (d) H_2O and C_2H_5OH ; $\Delta H_{soln} > 0$; $\Delta V_{sol} > 0$

Integer Answer Type

24. The freezing point of an aqueous solution of KCN containing $0.1892 \text{ mol kg}^{-1}$ was 0.74°C . On adding 0.095 mol of $Hg(CN)_2$, the freezing point of solution was -0.53°C . Assuming that complex is formed according to the equation



The value of m is

25. The solubility of pure nitrogen gas at 25°C and 1 atm is $6.8 \times 10^{-4} \text{ mol L}^{-1}$. The concentration of nitrogen dissolved in water under atmospheric conditions is 5.304×10^{-x} . The partial pressure of nitrogen gas in the atmosphere is 0.78 atm . The value of x is
26. The charge required for discharging 115 grams of Na from molten $NaCl$ in faradays is

Comprehension Type

At any fixed temperature, the vapour phase is always richer in more volatile component as compared to the solution phase. In other words, mole fraction of more volatile component is always greater in vapour phase than in solution phase. We can also say that vapour phase is relatively richer in the component whose addition to liquid mixture results in an increase in total vapour pressure.

27. If 2 moles of A and 3 moles of B are mixed to form an ideal solution, vapour pressures of A and B

are 120 and 180 mm of Hg respectively. The total vapour pressure of solution will be

- (a) 48 mm Hg (b) 108 mm Hg
 (c) 156 mm Hg (d) 15.6 mm Hg

28. The composition of A and B (mentioned in Q. 27) in the vapour phase when the first traces of vapour are formed is

- (a) $A = 0.407, B = 0.592$ (b) $A = 0.8, B = 0.1$
 (c) $A = 0.109, B = 0.791$ (d) $A = 0.307, B = 0.692$

Matrix Match Type

29. Match the entries listed in Column I with appropriate entries listed in Column II.

- | Column I | Column II |
|--|-------------------------------------|
| (A) Amount of urea to be dissolved in 500 mL of 0.1 N solution | (P) 3 g solute |
| (B) 1 L of 0.05 M propanol solution contains | (Q) 0.05 mole solute |
| (C) 100 g glucose in 10 g water | (R) Mole fraction of solute = 0.5 |
| (D) Pure water of density 1 g/mL | (S) Molality = 55.55 |

- | A | B | C | D |
|----------|------|------|------|
| (a) P | Q | R, S | S |
| (b) P, Q | P, Q | R, S | S |
| (c) P, Q | R, S | P, Q | R, S |
| (d) P, Q | R | R | R, S |

30. Match the entries listed in Column I with appropriate entries listed in Column II.

- | Column I | Column II |
|---------------------|---|
| (A) Mole fraction | (P) Mol/kg |
| (B) Hygroscopic | (Q) Depends on temperature |
| (C) Vapour pressure | (R) Independent of temperature |
| (D) Molality | (S) Solutions absorbing moisture from air |

- | A | B | C | D |
|-------|------|------|------|
| (a) R | P, S | Q | R |
| (b) Q | Q, S | R | P, R |
| (c) R | S | Q | P, R |
| (d) Q | S | P, Q | P |

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SELF CHECK

No. of questions attempted
 No. of questions correct
 Marks scored in percentage

Check your score! If your score is

- | | | |
|--------|--------------------------|--|
| > 90% | EXCELLENT WORK ! | You are well prepared to take the challenge of final exam. |
| 90-75% | GOOD WORK ! | You can score good in the final exam. |
| 74-60% | SATISFACTORY ! | You need to score more next time |
| < 60% | NOT SATISFACTORY! | Revise thoroughly and strengthen your concepts. |

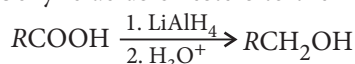


ADVANCED CHEMISTRY BLOC

(REDUCTIONS)

LITHIUM ALUMINIUM HYDRIDE, LiAlH_4

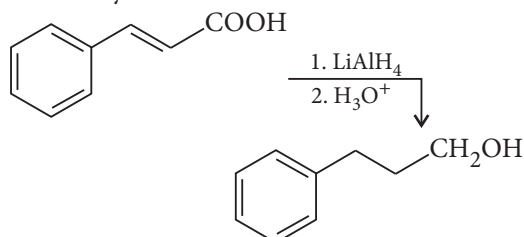
Lithium aluminium hydride is a very active reducing agent and is used particularly for the ready reductions of carboxylic acids or esters to their primary alcohols.



It also reduces :

- Acid chloride to alcohol
- Acid anhydride to alcohol
- Aldehyde to primary alcohol
- Ketone to secondary alcohol
- Amide to corresponding primary amine
- Aromatic nitro-hydrocarbons to azo compounds
- Aliphatic nitro compounds to primary amines

The $\text{C}=\text{C}$ double bond is usually unaffected. But in aromatic compounds the bond may be hydrogenated if it is directly linked to the aromatic nucleus.

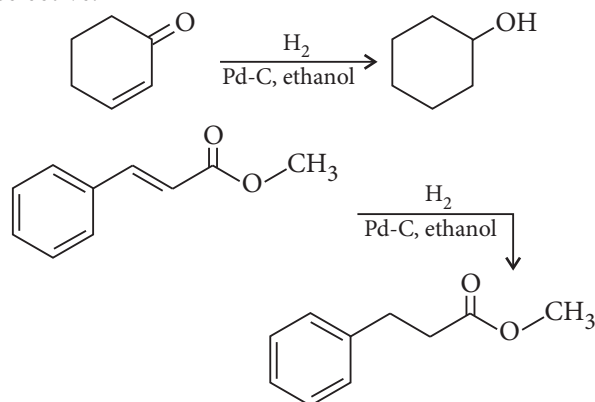


HYDROGENATION REACTION

Carboxylic esters may be hydrogenated more readily than the corresponding acids to primary alcohol. Nonetheless, such reactions require elevated temperature and pressure. Although yields of primary alcohols, corresponding to acyl fragment, are frequently excellent, such reductions are synthetically inconvenient. Hydrogenation using copper chromite at 60-200 atm pressure and 150-300°C are the most frequently employed conditions. Hydrogenation of ester using Raney-Nickel catalyst is particularly useful. Esters of both aliphatic and aromatic carboxylic acids may be hydrogenated to produce primary alcohols.

Ruthenium dioxide or ruthenium on carbon has given good results in the reduction of mono- and dicarboxylic acids to corresponding alcohols and glycols. Aromatic carboxylic acids can be reduced to alcohols without ring saturation.

Alkenes are much more reactive than most other unsaturated functional groups towards catalytic hydrogenation, and the reaction is therefore quite selective.



REDUCTION USING NaBH_4

Sodium borohydride is an effective reducing agent. It reduces :

- Aldehyde to primary alcohol
- Ketone to secondary alcohol
- Acid chloride to alcohol
- Epoxide to alcohol

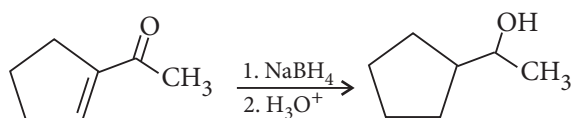
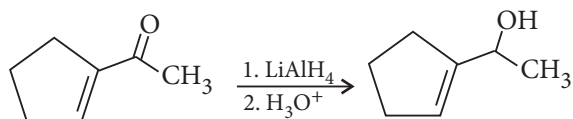
MPP-2 CLASS XII

ANSWER

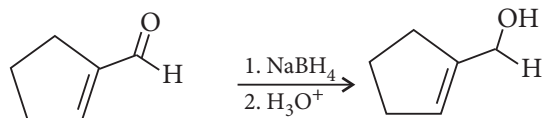
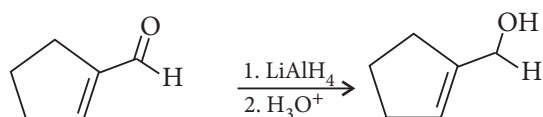
KEY

- | | | | | |
|-----------|-------------|-----------|---------|-------------|
| 1. (b) | 2. (b) | 3. (c) | 4. (b) | 5. (b) |
| 6. (d) | 7. (a) | 8. (d) | 9. (b) | 10. (c) |
| 11. (b) | 12. (c) | 13. (c) | 14. (c) | 15. (b) |
| 16. (c) | 17. (a) | 18. (a) | 19. (c) | 20. (a,c,d) |
| 21. (a,c) | 22. (a,c,d) | 23. (b,d) | 24. (2) | 25. (4) |
| 26. (5) | 27. (c) | 28. (d) | 29. (b) | 30. (c) |

But it fails to reduce carboxylic acids, esters and amides. It can reduce a double bond in conjugation with ketone as shown in the following case :

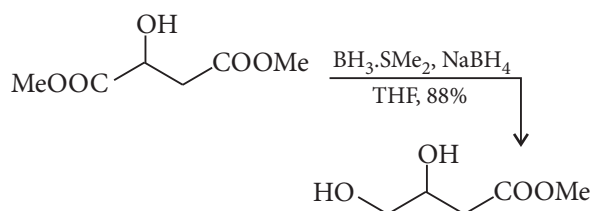


But this is not observed for aldehydes.



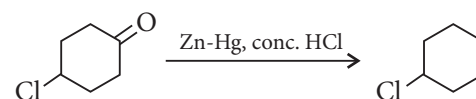
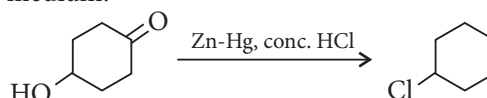
REDUCTION USING B_2H_6

Diborane at 0°C can slowly reduce carboxylic esters. Thus, this reagent is used to reduce chemoselectively aldehydes, ketones, amides or carboxylic acids in presence of esters. Diborane can reduce a double bond but cannot reduce acid chloride to alcohol,

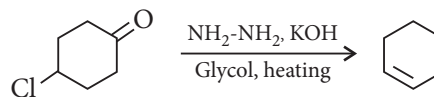
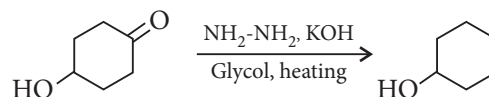


CLEMMENSEN AND WOLF—KISHNER REDUCTION

Clemmensen reduction reaction reduces carbonyl compounds in acid medium but Wolf—Kishner reduction reaction reduces carbonyl compound in basic medium.



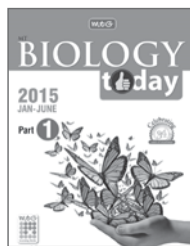
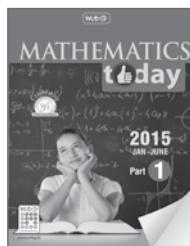
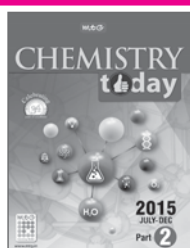
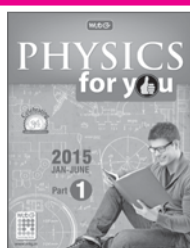
In acidic medium, the functional group $-\text{OH}$ also becomes $-\text{Cl}$.



In basic medium, elimination accompanies. So, these two reactions are compatible.



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SOLVED PAPER 2016

*Arunava Sarkar, West Bengal

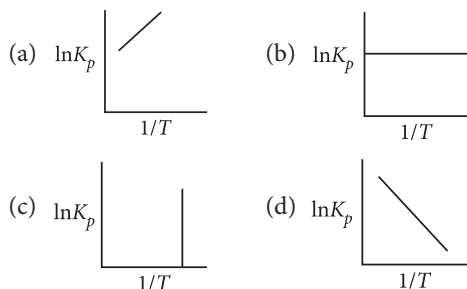
CATEGORY-I (Q. 1 to Q. 30)

Only one answer is correct. Correct answer will fetch full mark 1. Incorrect answer or any combination of more than one answer will fetch -1/4 marks.

- Which of the following statements regarding lanthanides is false?
 - All lanthanides are solid at room temperature.
 - Their usual oxidation state is +3.
 - They can be separated from one another by ion-exchange method.
 - Ionic radii of trivalent lanthanides steadily increases with increase in atomic number.
- Nitrogen dioxide is not produced on heating
 - KNO_3
 - $\text{Pb}(\text{NO}_3)_2$
 - $\text{Cu}(\text{NO}_3)_2$
 - AgNO_3
- The boiling points of HF, HCl, HBr and HI follow the order
 - $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$
 - $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$
 - $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
 - $\text{HCl} > \text{HF} > \text{HBr} > \text{HI}$
- In the solid state PCl_5 exists as
 - $[\text{PCl}_4]^-$ and $[\text{PCl}_6]^+$ ions
 - covalent PCl_5 molecules only
 - $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$ ions
 - covalent P_2Cl_{10} molecules only.
- Which statement is not correct for *ortho* and *para* hydrogen?
 - They have different boiling points.
 - Ortho*-form is more stable than *para*-form.
 - They differ in their nuclear spin.
 - The ratio of *ortho* to *para* hydrogen changes with change in temperature.
- The acid in which O—O bonding is present, is
 - $\text{H}_2\text{S}_2\text{O}_3$
 - $\text{H}_2\text{S}_2\text{O}_6$
 - $\text{H}_2\text{S}_2\text{O}_8$
 - $\text{H}_2\text{S}_4\text{O}_6$
- The metal which can be used to obtain metallic Cu from aqueous CuSO_4 solution is
 - Na
 - Ag
 - Hg
 - Fe
- If radium and chlorine combine to form radium chloride, the compound would be
 - half as radioactive as radium
 - twice as radioactive
 - as radioactive as radium
 - not radioactive.
- Which of the following arrangements is correct in respect of solubility in water?
 - $\text{CaSO}_4 > \text{BaSO}_4 > \text{BeSO}_4 > \text{MgSO}_4 > \text{SrSO}_4$
 - $\text{BeSO}_4 > \text{MgSO}_4 > \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$
 - $\text{BaSO}_4 > \text{SrSO}_4 > \text{CaSO}_4 > \text{MgSO}_4 > \text{BeSO}_4$
 - $\text{BeSO}_4 > \text{CaSO}_4 > \text{MgSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$
- The energy required to break one mole of hydrogen-hydrogen bonds in H_2 is 436 kJ. What is the longest wavelength of light required to break a single hydrogen-hydrogen bond?
 - 68.5 nm
 - 137 nm
 - 274 nm
 - 548 nm
- The correct order of O—O bond length in O_2 , H_2O_2 and O_3 is
 - $\text{O}_2 > \text{O}_3 > \text{H}_2\text{O}_2$
 - $\text{H}_2\text{O}_2 > \text{O}_3 > \text{O}_2$
 - $\text{O}_3 > \text{O}_2 > \text{H}_2\text{O}_2$
 - $\text{O}_3 > \text{H}_2\text{O}_2 > \text{O}_2$
- The number of σ and π -bonds between two carbon atoms in calcium carbide are
 - one σ , one π
 - one σ , two π
 - two σ , one π
 - one σ , $1\frac{1}{2}$ π
- An element E loses one α and two β -particles in three successive stages. The resulting element will be
 - an isobar of E
 - an isotone of E
 - an isotope of E
 - E itself.
- An element X belongs to fourth period and fifteenth group of the periodic table. Which of the following statements is true?
 - It has a completely filled s -orbital and a partially filled d -orbital.
 - It has completely filled s - and p -orbitals and a partially filled d -orbital.
 - It has completely filled s - and p -orbitals and a half-filled d -orbital.
 - It has a half-filled p -orbital and completely filled s - and d -orbitals.

* Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

15. Which of the following plots represents an exothermic reaction?



16. If P° and P are the vapour pressures of the pure solvent and solution and n_1 and n_2 are the moles of solute and solvent respectively in the solution then the correct relation between P and P° is

(a) $P^\circ = P \left[\frac{n_1}{n_1 + n_2} \right]$ (b) $P^\circ = P \left[\frac{n_2}{n_1 + n_2} \right]$
 (c) $P = P^\circ \left[\frac{n_2}{n_1 + n_2} \right]$ (d) $P = P^\circ \left[\frac{n_1}{n_1 + n_2} \right]$

17. Ionic solids with Schottky defect may contain in their structure

- (a) cation vacancies only
 (b) cation vacancies and interstitial cations
 (c) equal number of cation and anion vacancies
 (d) anion vacancies and interstitial anions.

18. The condition for a reaction to occur spontaneously is

- (a) ΔH must be negative
 (b) ΔS must be negative
 (c) $(\Delta H - T\Delta S)$ must be negative
 (d) $(\Delta H + T\Delta S)$ must be negative.

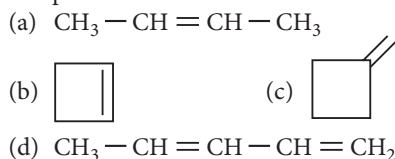
19. The order of equivalent conductance at infinite dilution for LiCl, NaCl and KCl is

- (a) $\text{LiCl} > \text{NaCl} > \text{KCl}$ (b) $\text{KCl} > \text{NaCl} > \text{LiCl}$
 (c) $\text{NaCl} > \text{KCl} > \text{LiCl}$ (d) $\text{LiCl} > \text{KCl} > \text{NaCl}$

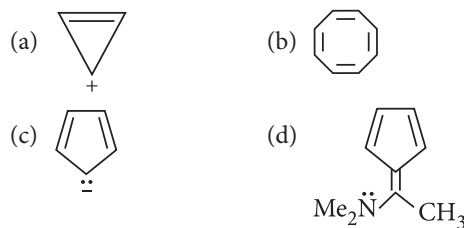
20. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 'S'. The corresponding solubility product is ' K_{sp} '. 'S' in terms of ' K_{sp} ' is given by the reaction

(a) $S = \left(\frac{K_{sp}}{128} \right)^{1/4}$ (b) $S = \left(\frac{K_{sp}}{256} \right)^{1/5}$
 (c) $S = (256 K_{sp})^{1/5}$ (d) $S = (128 K_{sp})^{1/4}$

21. Ozonolysis of an alkene produces only one dicarbonyl compound. The structure of the alkene is



22. From the following compounds choose the one which is not aromatic.



23. Amongst the following compounds, the one that will not respond to Cannizzaro reaction upon treatment with alkali is

- (a) Cl_3CCHO (b) Me_3CCHO
 (c) $\text{C}_6\text{H}_5\text{CHO}$ (d) HCHO

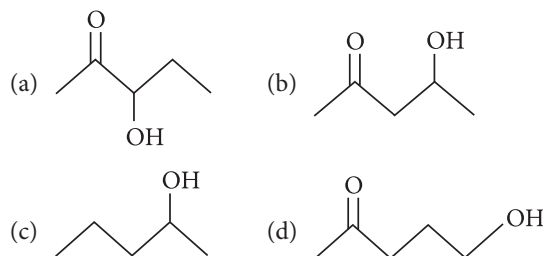
24. Which of the following compounds would not react with Lucas reagent at room temperature?

- (a) $\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$ (b) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (d) $(\text{CH}_3)_3\text{COH}$

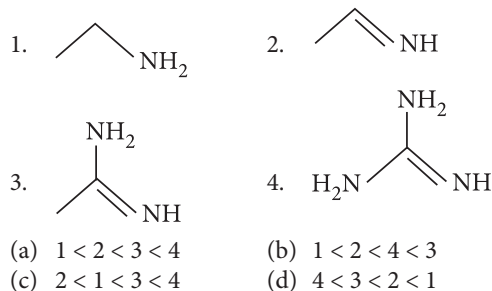
25. Amongst the following compounds the one which would not respond to iodoform test is

- (a) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (b) $\text{ICH}_2\text{COCH}_2\text{CH}_3$
 (c) CH_3COOH (d) CH_3CHO

26. Which of the following will be dehydrated most readily in alkaline medium?



27. The correct order of basicity of the following compounds is



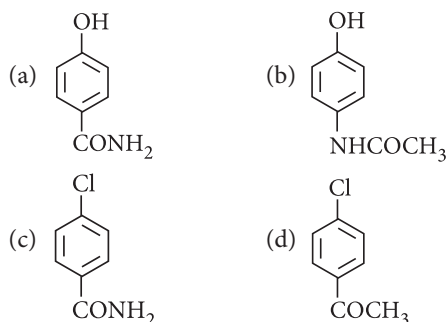
28. Which of the following reactions will not result in the formation of carbon-carbon bonds?

- (a) Cannizzaro reaction (b) Wurtz reaction
 (c) Reimer - Tiemann reaction
 (d) Friedel - Crafts acylation

29. Point out the false statement.

- (a) Colloidal sols are homogeneous
 (b) Colloids carry +ve or -ve charges
 (c) Colloids show Tyndall effect
 (d) The size range of colloidal particles is 10-1000 Å

30. The correct structure of the drug paracetamol is



CATEGORY-II (Q. 31 to Q. 35)

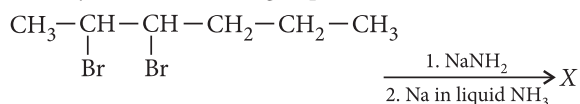
Only one answer is correct. Correct answer will fetch full marks 2. Incorrect answer or any combination of more than one answer will fetch -1/2 marks.

31. Compound X is tested and the results are shown in the table :

	Test	Result
*	Aqueous sodium hydroxide is added, then heated gently.	Gas given off which turns damp red litmus paper blue.
*	Dilute hydrochloric acid is added.	Effervescence, gas given off which turns lime water milky and acidified $K_2Cr_2O_7$ paper green.

Which ions are present in compound X?

- (a) Ammonium ions and sulphite ions
 (b) Ammonium ions and carbonate ions
 (c) Sodium ions and carbonate ions
 (d) Ammonium ions and sulphate ions
32. The time taken for an electron to complete one revolution in Bohr orbit of hydrogen atom is
- (a) $\frac{4m^2\pi r^2}{n^2h^2}$ (b) $\frac{n^2h^2}{4\pi mr^2}$
 (c) $\frac{4\pi^2mr^2}{nh}$ (d) $\frac{nh}{4\pi^2mr^2}$
33. Among the following, which should have the highest r.m.s. speed at the same temperature?
 (a) SO_2 (b) CO_2 (c) O_2 (d) H_2
34. The major products obtained during ozonolysis of 2,3-dimethyl-1-butene and subsequent reductions with Zn and H_2O are
 (a) methanoic acid and 2-methyl-2-butanone
 (b) methanal and 3-methyl-2-butanone
 (c) methanol and 2,3-dimethyl-3-butanone
 (d) methanoic acid and 2-methyl-3-butanone.
35. Identify X in the following sequence of reactions :

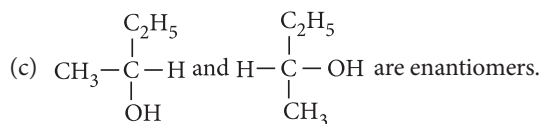


- (a) $CH_3-\underset{\substack{| \\ Br}}{CH}-\underset{\substack{| \\ NH_2}}{CH}-CH_2CH_2CH_3$
 (b) $\begin{array}{c} CH_3 \\ | \\ C=C \\ | \quad | \\ H \quad CH_2CH_2CH_3 \end{array}$
 (c) $\begin{array}{c} CH_3 \\ | \\ C=C \\ | \quad | \\ H \quad CH_2CH_2CH_3 \end{array}$
 (d) $CH_3-\underset{\substack{| \\ NH_2}}{CH}-\underset{\substack{| \\ NH_2}}{CH}-CH_2CH_2CH_3$

CATEGORY-III (Q. 36 TO Q. 40)

One or more answer(s) is (are) correct. Correct answer(s) will fetch 2. Any combination containing one or more incorrect answer will fetch 0 marks. If all correct answers are not marked and also no incorrect answer is marked than score = $2 \times$ number of correct answers marked/actual number of answers.

36. Which of the following statement(s) is (are) correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 ?
 (a) A deep red vapour is evolved.
 (b) The vapour when passed through NaOH solution, gives a yellow solution.
 (c) Chlorine gas is also evolved.
 (d) Chromyl chloride is formed.
37. Of the following molecules, which have shape similar to CO_2 ?
 (a) $HgCl_2$ (b) $SnCl_2$ (c) C_2H_2 (d) NO_2
38. In which of the following mixed aqueous solutions $pH = pK_a$ at equilibrium?
 (1) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M CH_3COONa
 (2) 100 mL of 0.1 M CH_3COOH + 50 mL of 0.1 M NaOH
 (3) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH
 (4) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NH_3
- (a) (1) is correct. (b) (2) is correct.
 (c) (3) is correct. (d) Both (1) and (2) are correct.
39. Amongst the following compounds, the one(s) which readily react with ethanolic KCN is
 (a) ethyl chloride (b) chlorobenzene
 (c) benzaldehyde (d) salicylic acid.
40. Choose the correct statement(s) among the following.
 (a) $\begin{array}{c} CH_3 \\ | \\ C=C \\ | \quad | \\ H \quad CH_3 \end{array}$ and $\begin{array}{c} H \\ | \\ C=C \\ | \quad | \\ H_3C \quad CH_3 \end{array}$ are enantiomers.
 (b) CH_3CHO on reaction with HCN gives racemic mixture.

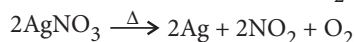
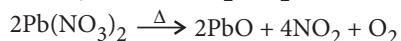
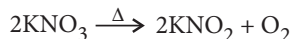


(d) $\text{CH}_3-\text{CH}=\text{NOH}$ shows geometrical isomerism.

SOLUTIONS

1. (d): Lanthanides contraction is that phenomenon where the ionic radii of trivalent lanthanides steadily decreases with increase in atomic number.

2. (a): Heating effects are as follow:



3. (b): Boiling point depends on the following factors:

- (1) Strong H-bonding that increases boiling point.
 - (2) van der Waals' force increases boiling point. van der Waals' force increases with increase in atomic radius.
 - (3) Increase in the molecular weight increases boiling point.
- Factors (2) and (3) give us the following order:



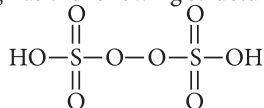
Factor (1) makes HF highest boiling point containing.

4. (c): In solid state, for PCl_5 , following observation is observed:



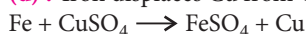
5. (b): *Ortho* hydrogen is more stable than *para* hydrogen at and above room temperature, whereas at low temperatures *para* hydrogen is more stable.

6. (c): $\text{H}_2\text{S}_2\text{O}_8$ has the following structure:



This is known as Marshall's acid. It contains O—O bond.

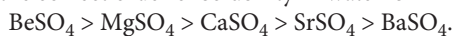
7. (d): Iron displaces Cu from CuSO_4 .



8. (c): Radioactivity remains same in free atom and if it is there in a compound.

9. (b): The solubilities of sulphates of alkaline earth metals decrease down the group because the hydration enthalpy decreases from Be^{2+} to Ba^{2+} appreciably as the size of the cation increases. As the sulphate ion is too big, the magnitude of lattice enthalpy almost remains constant on moving down the group.

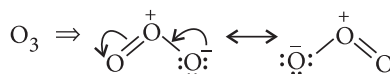
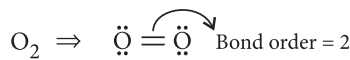
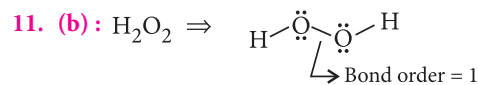
So, the correct order of solubility in water is



10. (c): Amount of energy required to break one H—H bond is

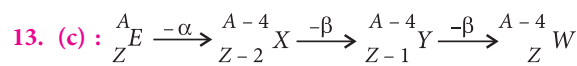
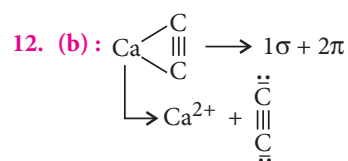
$$\frac{436 \times 10^3}{6.023 \times 10^{23}} = \frac{436}{6.023 \times 10^{20}} \text{ J mol}^{-1}$$

$$\begin{aligned} \text{Now, } E = \frac{hc}{\lambda} \therefore \lambda &= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{436} \times 6.023 \times 10^{20} \text{ m} \\ &= \frac{6.626 \times 6.023 \times 3}{436} \times 10^{-6} \approx 274 \text{ nm} \end{aligned}$$



$$\text{Bond order} = \frac{2+1}{2} = 1.5 \therefore \text{Order is } \text{O}_2 > \text{O}_3 > \text{H}_2\text{O}_2$$

Bond length is $\text{H}_2\text{O}_2 > \text{O}_3 > \text{O}_2$

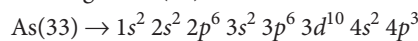


Both elements E and W have same atomic number but different mass numbers. Hence, both are isotopes. So, the resulting element will be an isotope of E .

14. (d): Element X belongs to fourth period and fifteenth group.

Period	1	2	3	4
Group 15	Nil	N(7)	P(15)	As(33)

Let us configure As(33). Now,



So, s and d -orbitals are fully-filled and p -orbital is half-filled.

15. (a): We have the following relationship.

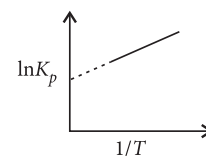
$$\ln K_p = -\frac{\Delta H}{RT} + \text{constant term}$$

Now, if ΔH is -ve, then the relation comes out to be:

$$\ln K_p = \frac{\Delta H}{RT} + \text{constant term}$$

$\therefore \ln K_p$ vs $\frac{1}{T}$ graph is similar to

$y = mx + c$ where, m and c both are positive. So, the graph will be as shown.



16. (c): We know according to Raoult's law,

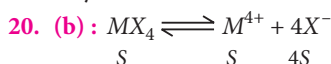
$$P = P^\circ \cdot x_{\text{solute}} \Rightarrow P = P^\circ \cdot \left[\frac{n_2}{n_1 + n_2} \right]$$

17. (c): In Schottky defect, equal number of cations and anions are missed from their lattice sites.

18. (c): For the spontaneity of a reaction, ΔG must be -ve. Now, $\Delta G = \Delta H - T\Delta S$

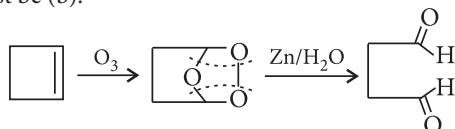
\therefore For a spontaneous reaction, $(\Delta H - T\Delta S)$ should be negative.

19. (b) : Li^+ , due to its high polarising power gets hydrated and its ionic mobility is reduced. Smaller the cation, higher is the hydration enthalpy and heavier becomes the cation. Mobility and conductance decrease.



$\therefore K_{sp} = [\text{M}^{4+}][\text{X}^-]^4 = S \cdot (4S)^4 = 256 S^5 \therefore S = \left(\frac{K_{sp}}{256}\right)^{1/5}$

21. (b) : As the product is only one dicarbonyl compound, it must be (b).

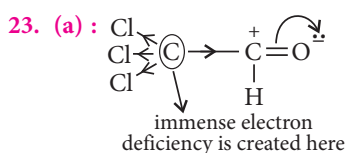


22. (b) : The following two points are must for a molecule to be aromatic :

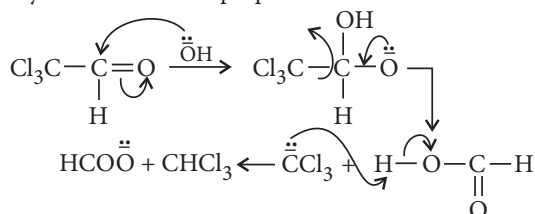
- (i) It must be planar.
- (ii) It must have $(4n + 2)$ delocalised electrons.

These are not fulfilled with (b).

\therefore (b) is not aromatic.



This is why CCl_3CHO is very much interested to undergo hydrolysis rather than disproportionation.

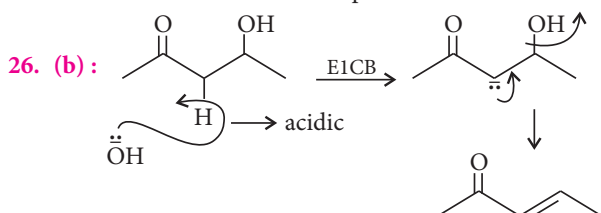


24. (c) : The order of reactivity of alcohols towards Lucas reagent is $3^\circ \text{ alcohol} > 2^\circ \text{ alcohol} > 1^\circ \text{ alcohol}$.

1° alcohols do not react with Lucas reagent at room temperature. It requires high temperature.

The benzyl and allyl alcohols react as rapidly as 3° alcohols with Lucas reagent because their cations are resonance stabilised and stable as 3° cations.

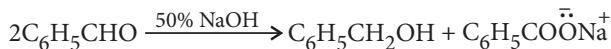
25. (c) : In acetic acid, the most acidic proton is attached to O-atom. So, deprotonation of α -hydrogen does not occur and hence no haloform reaction takes place.



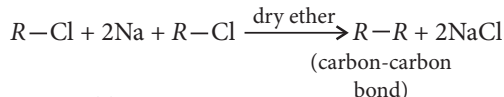
$\ddot{\text{O}}\text{H}$ is not a very good leaving group but expulsion of this becomes easy due to the conjugated structure.

27. (c)

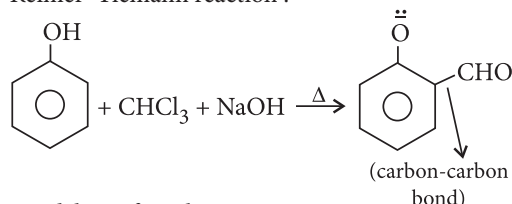
28. (a) : Cannizzaro reaction :



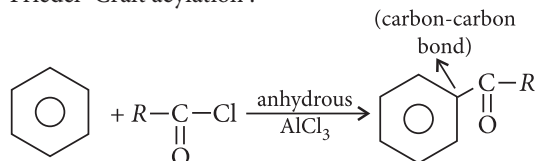
Wurtz reaction :



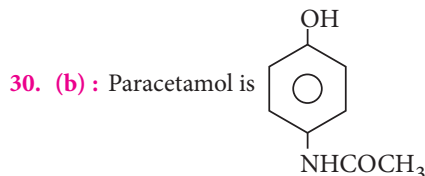
Reimer-Tiemann reaction :



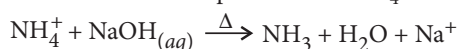
Friedel-Craft acylation :



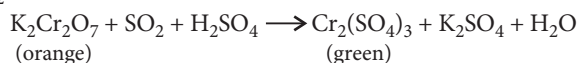
29. (a) : Colloidal sols are heterogeneous in nature.



31. (a) : In the first test, in presence of alkali, a gas with basic nature is evolved. This is possible with NH_4^+ salts.



For the second test, effervescence and turning lime water milky generally gives the idea of two gases: CO_2 and SO_2 . But as the gas turns acidified $\text{K}_2\text{Cr}_2\text{O}_7$ paper green so the gas should be SO_2 . Sulphite salts on reaction with dil. HCl evolves SO_2 .



32. (c) : We know according to Bohr's theory

$$mvr = \frac{nh}{2\pi}$$

(as the notations bear their usual meanings)

$$\Rightarrow v = \frac{nh}{2\pi mr}$$

\therefore Time required for one complete revolution,

$$T = \frac{2\pi r}{v} = \frac{2\pi r}{nh} 2\pi mr = \frac{4\pi^2 mr^2}{nh}$$

Contd. on Page No. 83

CHEMISTRY MUSING

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

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today. The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

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

PROBLEM Set 37

JEE MAIN/NEET

- The heat of hydrogenation of hex-1-ene is 126 kJ mol^{-1} . When a second double bond is introduced in the molecule, the heat of hydrogenation of the resulting compound is found to be 230 kJ mol^{-1} . The resulting compound will be
 - 1,5-hexadiene
 - 1,4-hexadiene
 - 1,3-hexadiene
 - 1,2-hexadiene.
- Two electrochemical cells are assembled in which the following reactions occur.

$$\text{V}^{2+} + \text{VO}^{2+} + 2\text{H}^+ \rightarrow 2\text{V}^{3+} + \text{H}_2\text{O}; E_{\text{cell}}^{\circ} = 0.616 \text{ V}$$

$$\text{V}^{3+} + \text{Ag}^+ + \text{H}_2\text{O} \rightarrow \text{VO}^{2+} + 2\text{H}^+ + \text{Ag}_{(s)};$$

$$E_{\text{cell}}^{\circ} = 0.439 \text{ V}$$

$$E^{\circ} \text{ for the half-cell reaction, } \text{V}^{3+} + e \rightarrow \text{V}^{2+} \text{ is}$$
 (Given : $E_{\text{Ag}^+/\text{Ag}}^{\circ} = 0.799 \text{ volt}$)
 - -0.256 V
 - $+0.256 \text{ V}$
 - $+1.055 \text{ V}$
 - -1.055 V
- In a molecule central atom 'A' has sp^3d hybridisation and surrounded by some σ bond pairs and some lone pairs. For this molecule three structures are possible. In each structure electron pair repulsion at 90° are given below :

Structure 1 : Lone pair/lone pair = 0; lone pair/bond pair = 6; bond pair/bond pair = 0

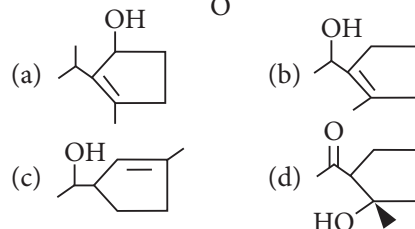
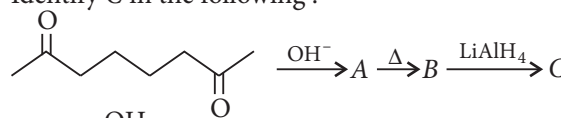
Structure 2 : Lone pair/lone pair = 1; lone pair/bond pair = 3; bond pair/bond pair = 2

Structure 3 : Lone pair/lone pair = 0; lone pair/bond pair = 4; bond pair/bond pair = 2

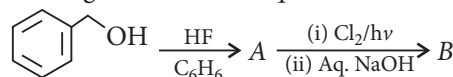
Molecule has maximum stability when it has

 - structure 1
 - structure 2
 - structure 3
 - both structure 2 and structure 3.

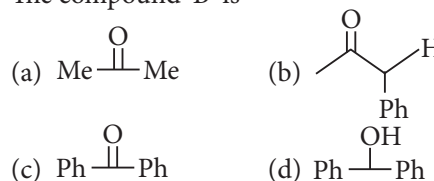
- Identify C in the following :



- In the given reaction sequence,



The compound 'B' is



JEE ADVANCED

- The half life of ^{32}P is 14.3 days. The specific activity of a phosphorus containing specimen having 1.0 part per million ^{32}P (Atomic weight of P = 31) is
 - 1.021 Ci/g
 - 0.242 Ci/g
 - 0.295 Ci/g
 - 1.043 Ci/g

COMPREHENSION

Inorganic compound (X) which produces green colour on flame. (X) also produces a colourless gas (G) and colourless solution (S) with dil. CH_3COOH . Solution (S) produces white ppt. with Na_2SO_4 but does not produce

ppt. with NaCl. Gas (G) produces black ppt. with AgNO₃ solution.

7. $X \xrightarrow{\text{on heating with BaSO}_4}$ Residue + gas G'
 Select incorrect statement about gas G'.
 (a) It is triatomic.
 (b) It produces yellowish-white ppt. with gas G in aq. solution.
 (c) It produces water soluble salt with KOH solution.
 (d) It produces black ppt. with AgNO₃ solution.
8. Resulting solution (S) in CH₃COOH_(aq.) produces ppt. with
 (a) Na₂S (b) K₂CrO₄
 (c) (NH₄)₂C₂O₄ (d) KI

Contd. from Page No. 81

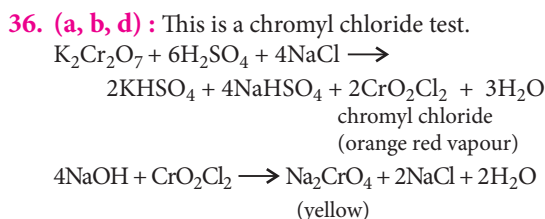
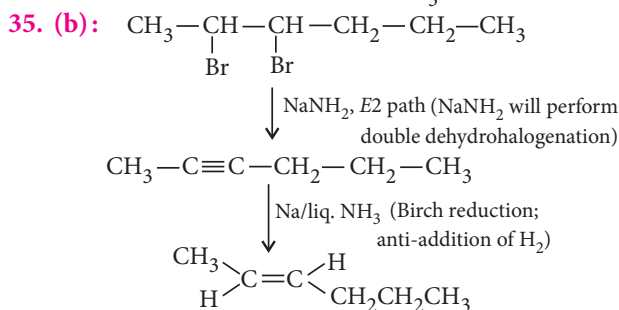
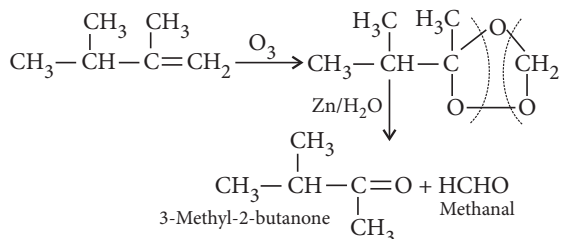


33. (d): We know, r.m.s. speed $(c) = \sqrt{\frac{3RT}{M}}$

So, if temperature remains the same, $c \propto \frac{1}{\sqrt{M}}$

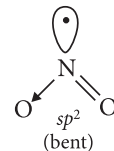
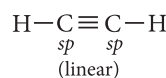
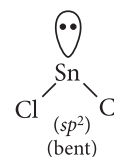
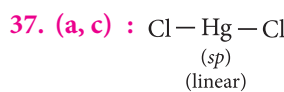
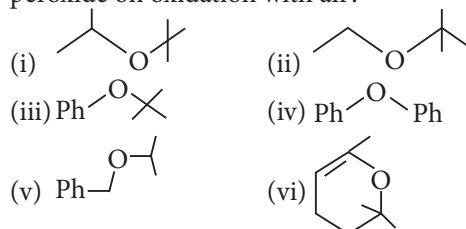
So, gas with least molecular weight will have the highest r.m.s. speed.

34. (b): 2,3-Dimethyl-1-butene has the following structure :



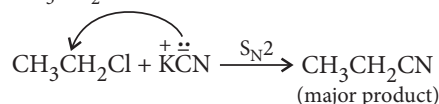
INTEGER VALUE

9. A 40 mL solution of a weak base, BOH, is titrated with 0.1 N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after the addition of 5 mL and 20 mL of the acid respectively. The dissociation constant of the base is 1.82×10^{-x} . The value of x is
10. How many of the following ethers give(s) ether peroxide on oxidation with air?



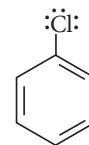
38. (a, b, d)

39. (a, c) : $\ddot{\text{C}}\text{N}^-$ is a very good nucleophile. With this concept, KCN can react with 1° halide i.e. CH₃CH₂Cl to give CH₃CH₂CN.

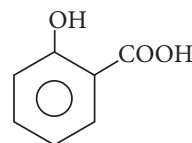


$\ddot{\text{C}}\text{N}^-$ is a very good nucleophile and a very good leaving group, with this concept $\overset{+}{\text{C}}\ddot{\text{N}}^-$ reacts with benzaldehyde to carry

Benzoin condensation to give $\text{Ph} - \underset{\text{OH}}{\text{CH}} - \overset{\text{O}}{\parallel} \text{C} - \text{Ph}$.



Chlorobenzene is inert to KCN because a partial double bond character is produced between chlorine and benzene ring due to resonance.



Salicylic acid has nothing to do with $\ddot{\text{C}}\text{N}^-$ of KCN.

40. (b, d)



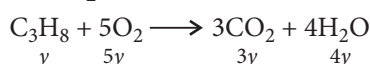
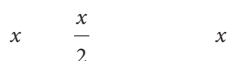
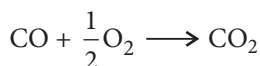
CHEMISTRY MUSING

SOLUTION SET 36

1. (c): Volume of gaseous mixture = 12 mL
 Volume of O₂ added = 25 mL
 Let volume of CO be x mL and that of C₃H₈ be y mL
 Contraction in volume = 15 mL
 \therefore Volume of N₂ = (12 - x - y) mL
 \therefore Volume of mixture after combustion

$$= 12 + 25 - 15 = 22 \text{ mL}$$

Volume of CO₂ absorbed after passing through KOH
 $= 22 - 4 = 18 \text{ mL}$



$$\text{Contraction} = x + \frac{x}{2} - x + y + 5y - 3y = \frac{x}{2} + 3y$$

$$\text{Hence, } \frac{x}{2} + 3y = 15 \quad \dots(\text{i})$$

Volume of CO₂ liberated on combustion which is absorbed by KOH = $x + 3y$

$$\therefore x + 3y = 18 \quad \dots(\text{ii})$$

Solving eq. (i) and eq. (ii), we get

$$x = 6 \text{ mL and } y = 4 \text{ mL}$$

\therefore Volume of CO = $x = 6$ mL, Volume of C₃H₈ = $y = 4$ mL

Volume of N₂ = 12 - x - y = 12 - 6 - 4 = 2 mL

$$\%(\text{CO}) = \frac{6}{12} \times 100 = 50\%; \quad \%(\text{C}_3\text{H}_8) = \frac{4}{12} \times 100 = 33.33\%$$

$$\%(\text{N}_2) = \frac{2}{12} \times 100 = 16.67\%$$

2. (a): Let N_1 be the normality of acid mixture and volume of H₂SO₄ be x mL.

Using the normality equation,

$$(25 \times 2 + 50 \times 4 + x \times 5 \times 2) = 1000 N_1$$

$$(50 + 200 + 10x) = 1000 N_1 \quad \dots(\text{i})$$

Also, [50 mL (N_1)] acid mixture = [25 mL (1 N)] alkali

$$\therefore N_1 = \frac{1}{2} \quad \dots(\text{ii})$$

$$\text{From equations (i) and (ii), } (250 + 10x) = 1000 \times \frac{1}{2}$$

$$\Rightarrow 250 + 10x = 500 \Rightarrow x = 25.0 \text{ mL}$$

3. (c): Weaker the acid, lower is the value of dissociation constant. Br in option (c) shows least -I-effect thus, it is the weakest acid.

4. (a): Number of atoms in 1 kg or 1000 g of ¹³⁹La

$$= \frac{1000 \text{ g}}{139 \text{ g}} \times 6 \times 10^{23} = \frac{6}{139} \times 10^{26}$$

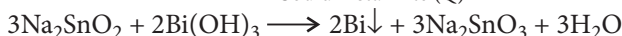
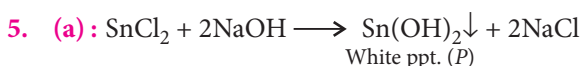
$$\begin{aligned} \therefore \text{ Number of radioactive } ^{138}\text{La atoms, } N &= 0.1\% \text{ of number of atoms of } ^{139}\text{La} \\ &= \frac{0.1}{100} \times \frac{6}{139} \times 10^{26} = \frac{6}{139} \times 10^{23} \end{aligned}$$

Decay constant,

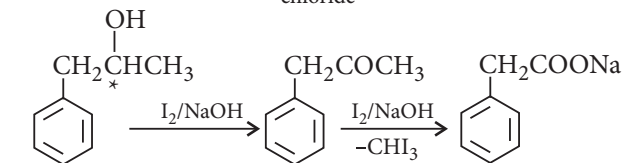
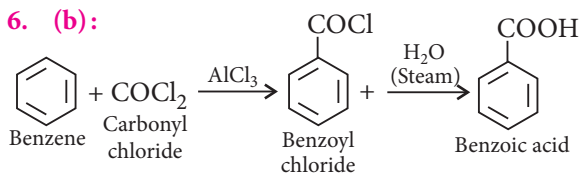
$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693 \text{ s}^{-1}}{1.1 \times 10^{10} \times 365.25 \times 24 \times (60)^2}$$

$$\therefore \text{ Rate of decay, } R = -\frac{dN}{dt} = \lambda N$$

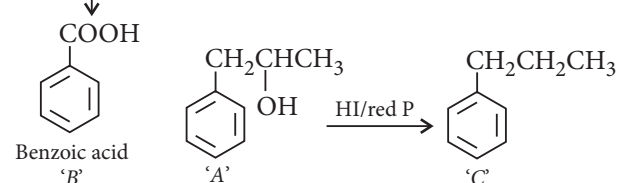
$$= \frac{0.693}{1.1 \times 10^{10} \times 365.25 \times 24 \times 60 \times 60} \times \frac{6}{139} \times 10^{23} = 8617 \text{ s}^{-1}$$



6. (b):



KMnO₄ ↓ KOH, heat

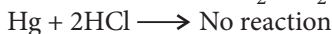
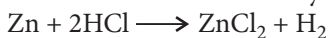


Molecular weight of 'C' (C₆H₅CH₂CH₂CH₃) is 12 × 9 + 12 = 108 + 12 = 120 g mol⁻¹.

7. (b): P = Zn, P₁ = Zn(NO₃)₂, P₂ = Zn²⁺
 P₃ = Na₂ZnO₂ or Na₂[Zn(OH)₄], Q = Hg
 Q₁ = Hg₂(NO₃)₂, Q₂ = Hg₂I₂ (Green ppt.),
 Q₃ = K₂[HgI₄], P₄ = Zn₂[Fe(CN)₆]₂²⁻ or K₂Zn₃[Fe(CN)₆]₂
 K₂HgI₄ produces brown ppt. with NH₄⁺ ion.

Brown ppt. = HgO · Hg $\begin{matrix} \diagup \text{NH}_2 \\ \diagdown \text{I} \end{matrix}$

8. (a): Zn and Hg with HCl is used in Clemmensen reduction. ZnO is thermally more stable than HgO.



9. (7)

10. (3): (a), (b) and (e) are oxidation reactions. ◇◇

CROSSWORD



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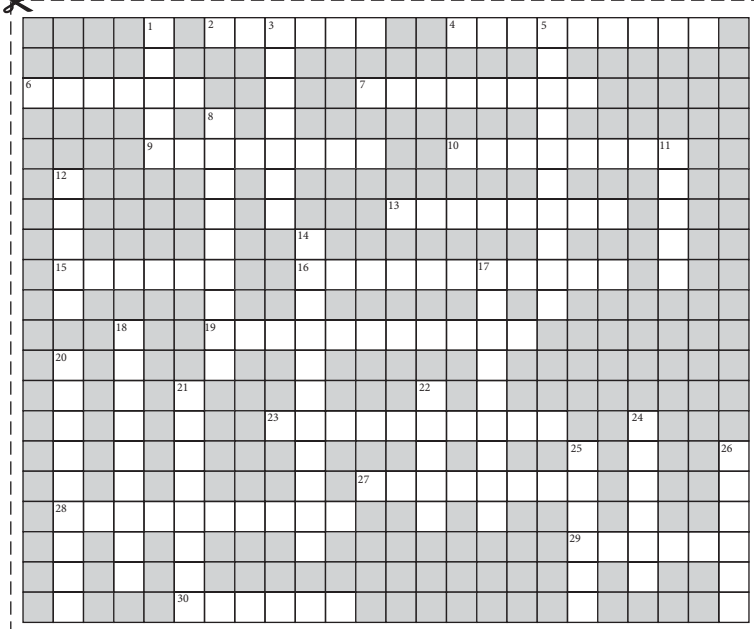
ACROSS

2. The chief storage polysaccharide of plants. (6)
4. Coordinate complexes of ethers with Lewis acids. (9)
6. The quantum of thermal energy emitted when transition takes place from higher vibrational state to a lower vibrational state in solids. (6)
7. Substances which neutralise the excess hydrochloric acid and raise the pH to an appropriate level in stomach. (8)
9. Element used in optophone. (8)
10. The mixture of metallic oxide and aluminium powder in the ratio of 3 : 1. (8)
13. Tetra substituted vicinal glycols. (8)
15. The pressure developed inside the cell due to inflow of water. (6)
16. Stability constant of a complex is the reciprocal of the _____ constant. (11)
19. The process which involves the replacement of a H-atom of thiol group by the nitroso group. (11)
23. Titration in which reducing agents are directly titrated against iodine as the oxidising agent in neutral or slightly acidic medium. (10)
27. The substance which forms cathode in dry cell. (8)
28. Nucleophilic substitution reactions in which the solvent acts as the nucleophile. (10)
29. Shape of azide ion. (6)
30. The cubic structure of ferrite. (6)

DOWN

1. Infusible impurity leftover during liquation. (5)
3. Class of organic compounds formed on reaction of carboxylic acids with HI and red phosphorus at 473 K. (7)
5. Reactions which are accompanied by increase of free energy. (10)
8. The particles constituting the cathode rays. (9)
11. The number of tetrahedral voids in fcc unit cell. (5)
12. Allotrope of phosphorus which causes phosphy jaw. (5)

Cut Here



14. Salt that is prepared by dissolving equimolar amounts of Na_2HPO_4 and NH_4Cl in water followed by concentration and crystallisation. (11)
17. Two compounds with similar chemical composition in the same crystalline form. (9)
18. Hydrogen peroxide is used as an _____ to remove traces of chlorine and hypochlorite. (9)
20. Temperature at which gas shows neither cooling effect nor heating effect. (9)
21. A class of proteins, found in combination with nucleic acid and are present in RBCs. (8)
22. The cyclic product that is obtained by addition of ethylene glycol to a ketone. (5)
24. Fluorochlorobromocarbons used as fire fighting in tanks and armoured personnel carrier. (6)
25. Colour of methyl red in basic solutions. (6)
26. Polymers in which the intermolecular forces of attraction are the strongest. (6)



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