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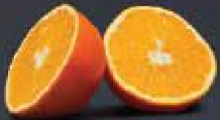

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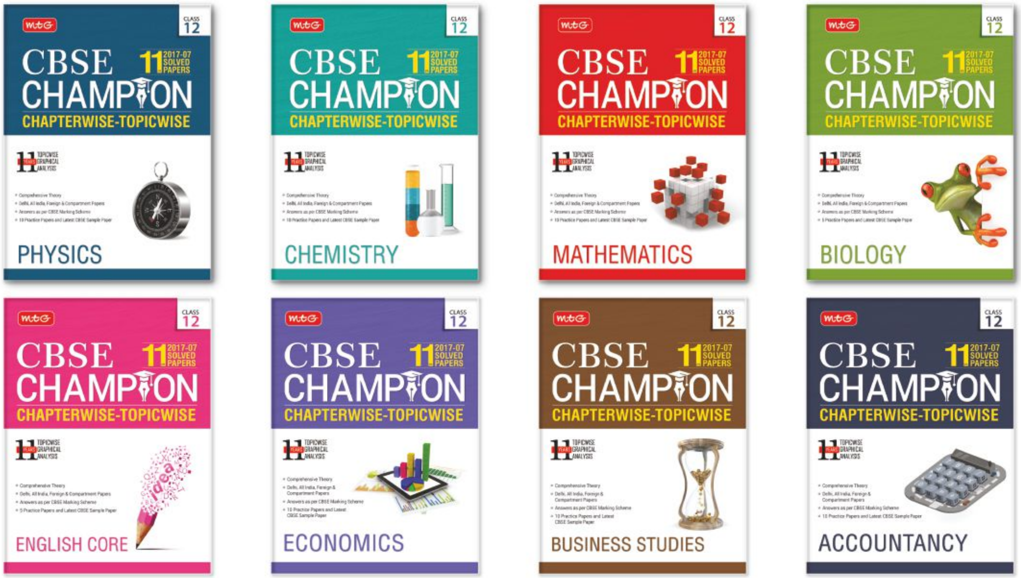
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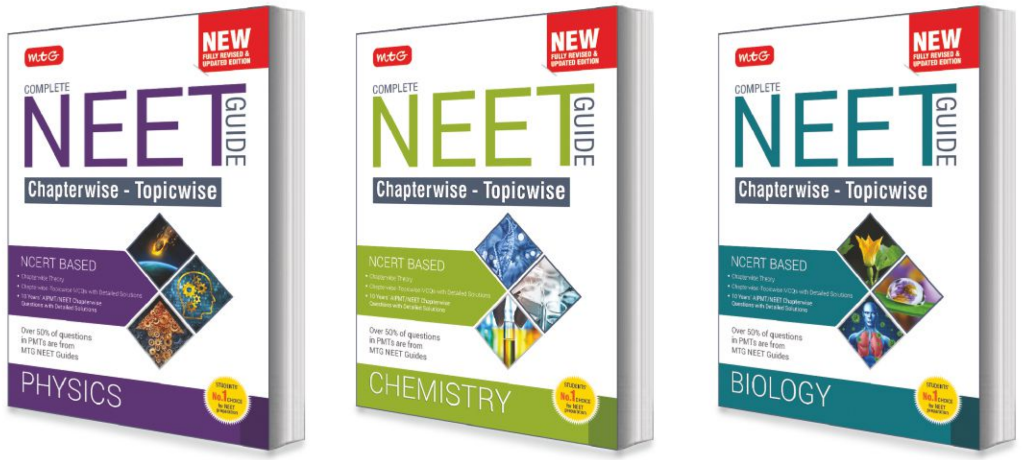
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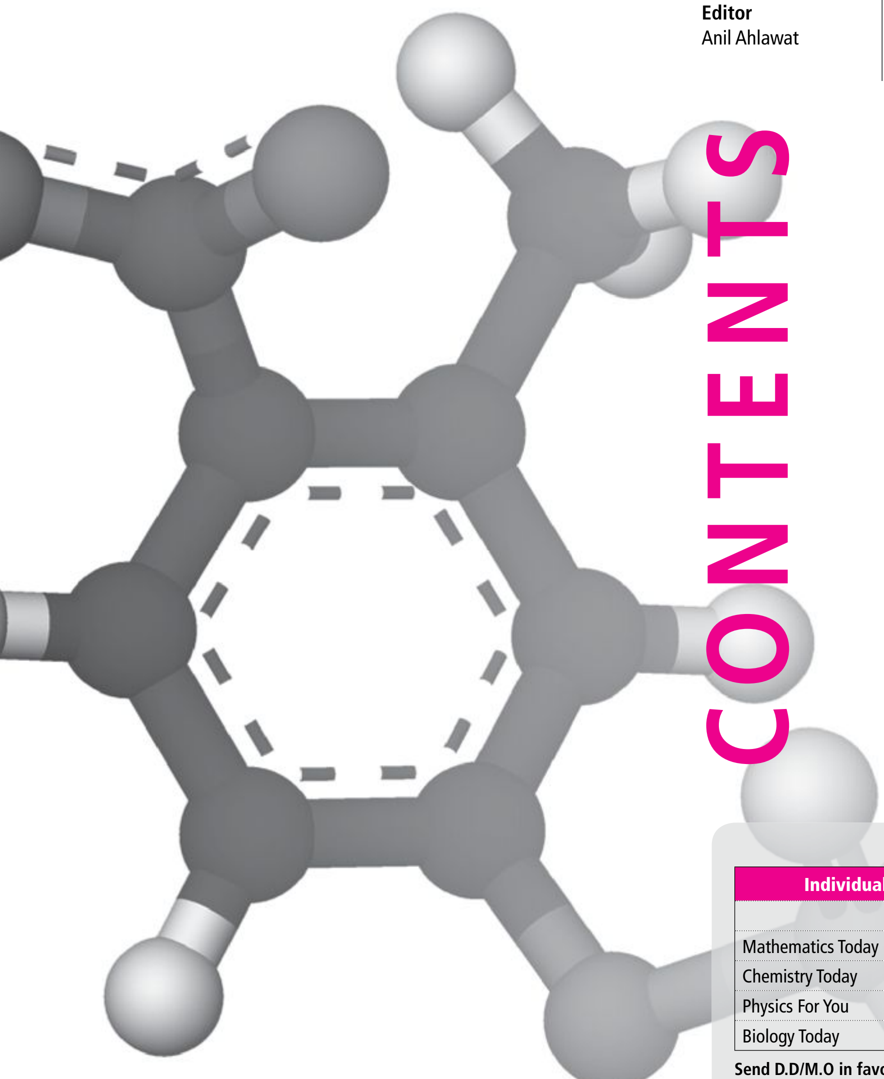

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Unit 2 CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES | CHEMICAL BONDING AND MOLECULAR STRUCTURE

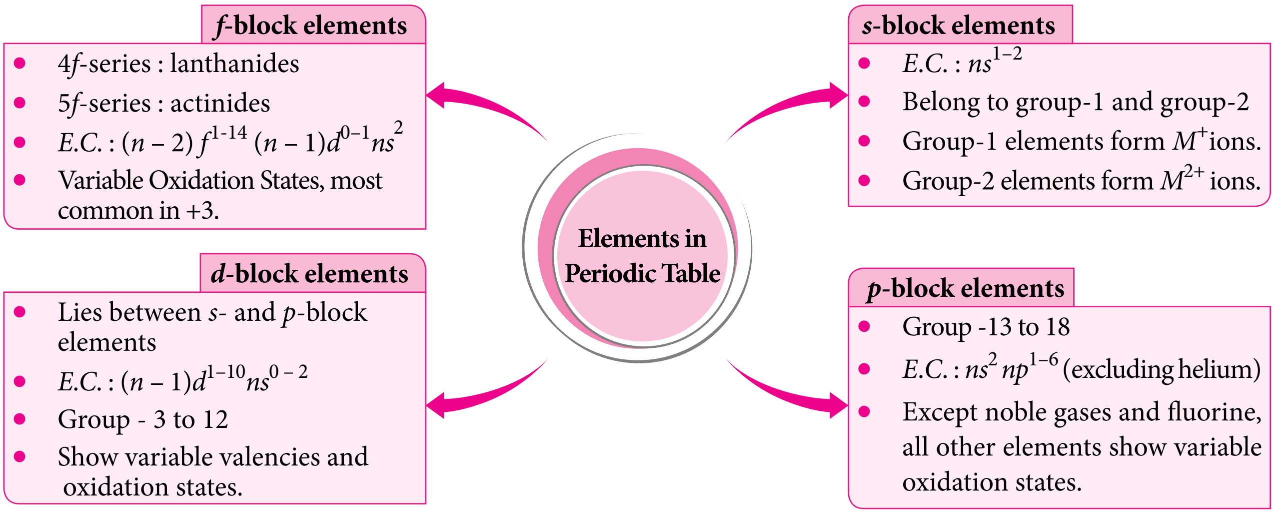
CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

MODERN PERIODIC LAW

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

FEATURES OF MODERN PERIODIC TABLE

- Elements are arranged in order of increasing atomic numbers.
- It has seven horizontal rows known as periods.
- There are eighteen vertical columns which are called groups or families.



Elements in Periodic Table

***f*-block elements**

- 4*f*-series : lanthanides
- 5*f*-series : actinides
- E.C. : $(n-2)f^{1-14}\,(n-1)d^{0-1}ns^2$
- Variable Oxidation States, most common in +3.

***s*-block elements**

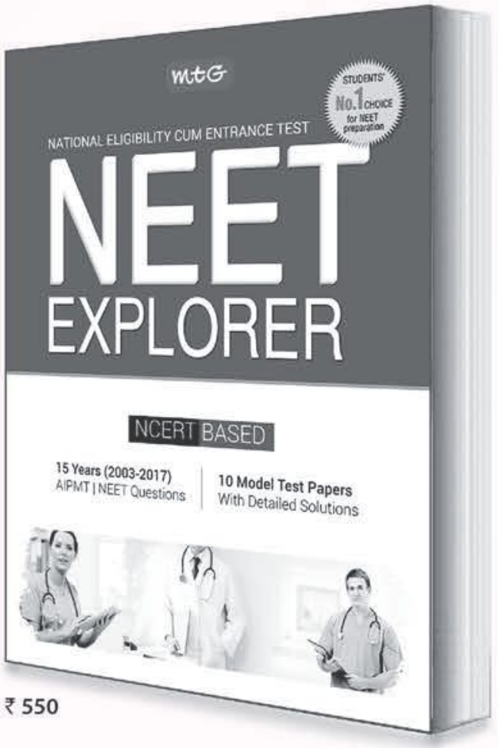
- E.C. : ns^{1-2}
- Belong to group-1 and group-2
- Group-1 elements form M^+ ions.
- Group-2 elements form M^{2+} ions.

***d*-block elements**

- Lies between *s*- and *p*-block elements
- E.C. : $(n-1)d^{1-10}ns^{0-2}$
- Group - 3 to 12
- Show variable valencies and oxidation states.

***p*-block elements**

- Group -13 to 18
- E.C. : $ns^2\,np^{1-6}$ (excluding helium)
- Except noble gases and fluorine, all other elements show variable oxidation states.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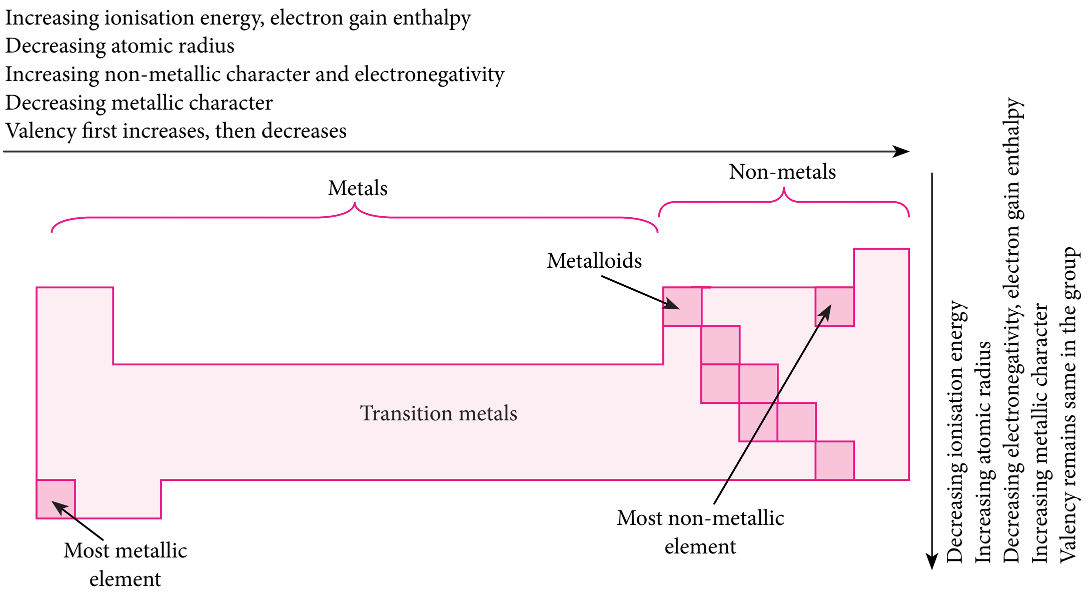
TRENDS IN PROPERTIES OF ELEMENTS



Ionic Radius

- The effective distance from the centre of nucleus of an ion upto which it has an influence on its electron cloud is called its ionic radius.

  $$d_{(a^+ - b^-)} = r_{a^+} + r_{b^-}$$

  Radii of isoelectronic ions,

  $$r_{\text{anion}} > r_{\text{neutral}} > r_{\text{cation}}$$

  $$\text{Ionic radius} \propto \frac{1}{\text{Effective nuclear charge}}$$

Ionisation Enthalpy

- The amount of energy required to remove the most loosely bounded electrons from an isolated gaseous atom in its ground state, is called ionisation enthalpy

  $$M_{(g)} \xrightarrow{\text{Energy}} M^+_{(g)} + e^-$$

  $$\text{Ionisation energy} \propto \frac{1}{\text{Size of atom}} \propto \text{Effective nuclear charge}$$

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

  $$\text{First ionisation energy} < \text{Second ionisation energy} < \text{Third ionisation energy}$$

Electron Gain Enthalpy

- It is the molar enthalpy change when an neutral isolated gaseous atom in its ground state gains an electron to form the corresponding anion.

  $$X_{(g)} + e^- \longrightarrow X^-_{(g)}$$

  For elements with stable electronic configuration, electron gain enthalpy is zero or nearly zero.

Electronegativity

- The relative tendency of an atom in a molecule to attract the shared pair of electrons towards itself in a covalent bond is termed as electronegativity.

  $$E.N. \propto \frac{1}{\text{Atomic size}} \propto I.E.$$

  Flourine is most electronegative atom.
- Mulliken scale of electronegativity,

  $$\chi = \frac{1}{2}[\Delta_i H + \Delta_{eg} H]$$
- Pauling scale of electronegativity,

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

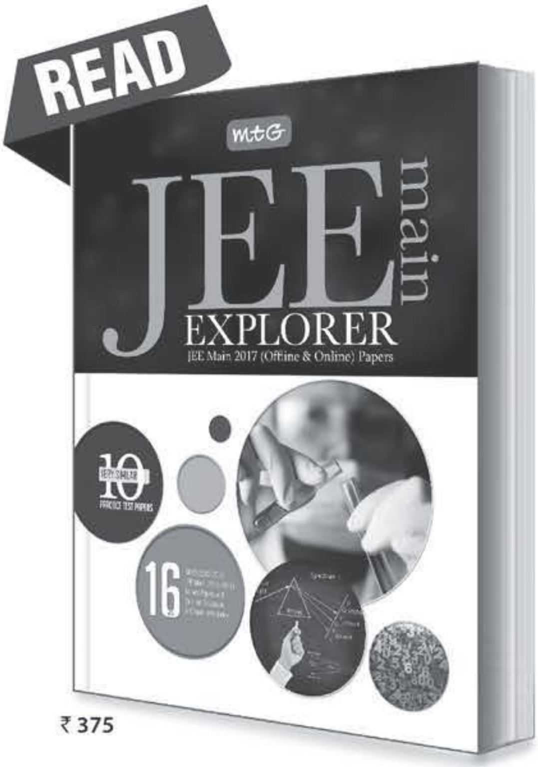
  where, $\Delta = E_{A-B} - \frac{1}{2}\sqrt{E_{A-A} + E_{B-B}}$

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

INFOSHOTS

Mythological reference!

There are 15 elements named after a mythological character or reference. Thorium and vanadium are named after Norse God of war 'Thor' and Goddess of beauty 'Vanadis', respectively. Helium is named after the Sun God 'Helios', irridium after Goddess of rainbow 'Iris', and titanium after the 'Titans'.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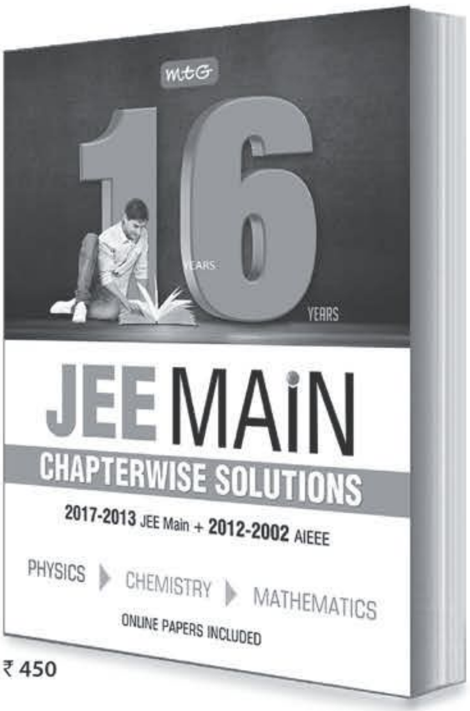
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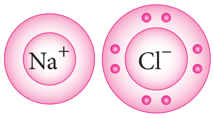
CHEMICAL BONDING AND MOLECULAR STRUCTURE

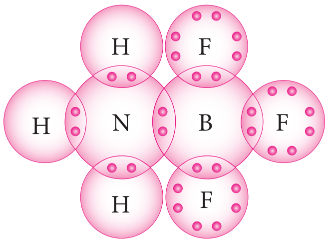
TYPES OF BONDS

Bonds

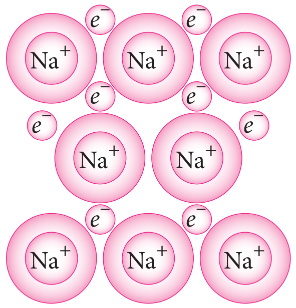
Ionic bond
Electrostatic attraction between a cation (metal) and an anion (non-metal).



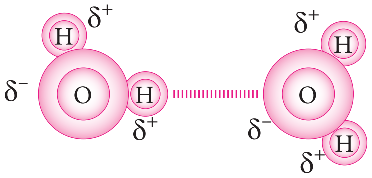
Coordinate bond
Coordinate bonds are formed between electron deficient molecules or ions (Lewis acids) and electron rich molecules or ions (Lewis bases).



Metallic bond
Attraction between mobile electrons and positively charged metallic atoms.



Hydrogen bond
Bond between H-atom and electronegative elements (like N, O, F)

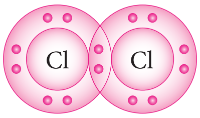


Intermolecular
e.g., HF, H_2O

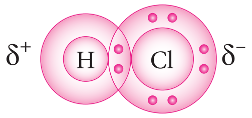
Intramolecular
e.g., *o*-Nitrophenol

Covalent bond
Bond between non-metal atoms due to sharing of electron pairs.

Non-polar covalent



Polar covalent



- **Formal charge on an atom** = Total number of valence electrons in an atom – Total number of lone pairs of electrons – $\frac{1}{2}$ (Total number of shared electrons).

VSEPR THEORY

- It states that bonded atoms in a molecule adopt that particular arrangement in space, in which electron pairs surrounding the central atom repel one another and go far apart so, there are no further repulsions.
- The magnitude of repulsion is : $lp - lp > lp - bp > bp - bp$
- Shape of the molecule is determined by this theory.

Geometry Based on VSEPR Theory

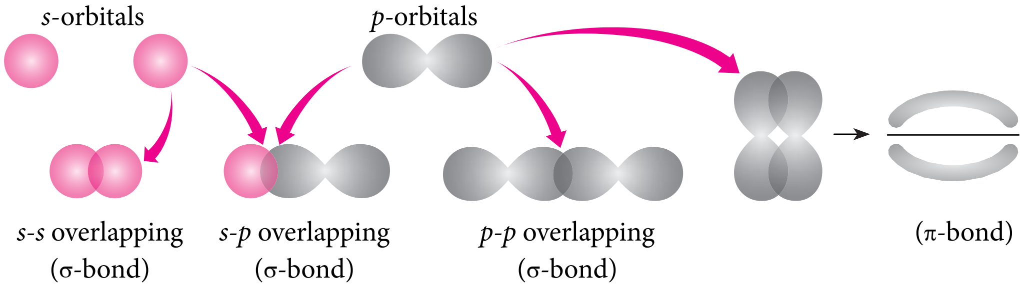
Total number of electron pairs	Molecular formula	Geometry	Bond angle	Example
2	AX_2	Linear	180°	$BeCl_2$
3	AX_3 AX_2E	Trianglar planar Bent (V-shape)	120° 119°	BF_3 SO_2

4	AX_4	Tetrahedral	109°28′	CH_4, SiH_4
	AX_3E	Trigonal pyramidal	107°48′	NH_3
	AX_2E_2	Bent	104°27′	H_2O
5	AX_5	Trigonal bipyramidal	120 and 90°	PCl_5
	AX_4E	Irregular tetrahedral (Sea saw)	101°36′ and 86°33′	SF_4 and IF_4^+
	AX_3E_2	T-shaped	87°40′	ClF_3
	AX_2E_3	Linear	180°	I_3^-
6	AX_6	Octahedral	90°	SF_6
	AX_5E	Square pyramidal	84° 30′	BrF_5
	AX_4E_2	Square planar	90°	XeF_4
7	AX_7	Pentagonal bipyramidal	72° 90′	IF_7

VALENCE BOND THEORY (VBT)

- The formation of covalent bond is due to pairing of electrons present in the valence shell having opposite spin.

Overlapping of Atomic Orbitals



Hybridisation

- The intermixing of atomic orbitals of same energy or slightly different energy to produce entirely new sets of orbitals of equivalent energies and identical shapes.
- The structure of any molecule can be predicted on the basis of hybridisation by using formula :

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

$$\Rightarrow \quad H = \frac{1}{2}[V + M - c + a]$$

MOLECULAR ORBITAL THEORY (MOT)

- Atomic orbitals of comparable energies combine to form molecular orbitals.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals.
- When two atomic orbitals combine, two molecular orbitals are formed, one with lower energy (bonding molecular orbital) another with high energy (antibonding molecular orbital).

INFO SHOTS

Chemical bonding in metal borides!

Ultrahard materials, such as TiB_2, ReB_2 and OsB_2 are being developed as potential lower cost alternatives to diamond, carbides and boron-nitride that are traditionally used for cutting, drilling and polishing tools.

Order of Energy

- For O_2 and F_2,
  $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$
- For Li_2 to N_2,
  $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$
- Bond order = $\frac{1}{2}(N_b - N_a)$

  $\because$ N_b = Number of electrons in bonding molecular orbitals,

  N_a = Number of electrons in antibonding molecular orbitals.
- Bond strength $\propto$ Bond order $\propto \frac{1}{\text{Bond length}}$

SPEED PRACTICE

1. Anhydrous $AlCl_3$ is covalent but hydrated $AlCl_3.6H_2O$ is ionic because
   (a) $AlCl_3$ dissolves in CS_2
   (b) $AlCl_3$ has planar structure
   (c) *I.E.* of Al is low
   (d) hydration energy of Al compensates the *I.E.*

2. Atomic number 64 will have electronic configuration
   (a) $[Xe]_{54}\,6s^2\,4f^8$ (b) $[Xe]_{54}\,6s^2\,4f^7\,5d^1$
   (c) $[Xe]_{54}\,4f^{10}$ (d) $[Xe]_{54}\,6s^2\,4f^7\,5p^1$

3. The correct order for bond angle in following is
   (a) $NH_2^- > NH_3 > NH_4^+$
   (b) $NH_4^+ > NH_2^- > NH_3$
   (c) $NH_4^+ > NH_3 > NH_2^-$
   (d) $NH_3 > NH_4^+ > NH_2^-$

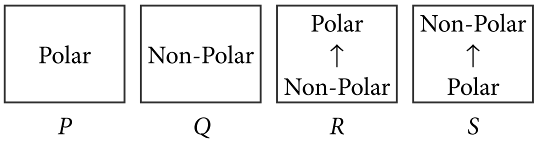
4. Ionic radii of
   (a) $Ti^{4+} < Mn^{2+}$ (b) $^{35}Cl^- < ^{37}Cl^-$
   (c) $K^+ > Cl^-$ (d) $P^{3+} > P^{5+}$

5. 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)**

6. Consider the following statements :
   1. Cs^+ is more highly hydrated than the other alkali metal ions.
   2. Among the alkali metals Li, Na, K and Rb, lithium has the highest melting point.
   3. Among the alkali metals only lithium forms a stable nitride by direct combination.

   Out of these statements
   (a) 1, 2 and 3 are correct
   (b) 1 and 2 are correct
   (c) 1 and 3 are correct
   (d) 2 and 3 are correct.

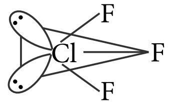
7. If climbing of water droplets is made to occur on a coated microscope slide, the slide would have to be coated in which of the following way



   (a) *P* (b) *Q* (c) *R* (d) *S*

8. The electronic configuration of the element is $1s^2\,2s^2\,2p^6\,3s^2\,3p^3$. What is the atomic number of the element which is just below the above element in the periodic table?
   (a) 33 (b) 34 (c) 31 (d) 49

9. Which geometry of ClF_3 is more stable ?

1.


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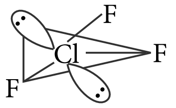

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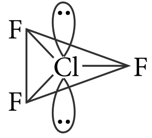


   (a) Only 2, 3 (b) Only 1
   (c) Only 3 (d) Only 2

10. Among the following the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by

(a) $MnSO_4.4H_2O$ (b) $CuSO_4.5H_2O$
(c) $FeSO_4.6H_2O$ (d) $NiSO_4.6H_2O$

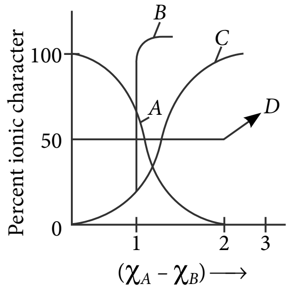
11. CO is practically non-polar since
(a) the σ-electron drift from C to O is almost nullified by the π-electron drift from O to C
(b) the σ-electron drift from O to C is almost nullified by the π-electron drift from C to O
(c) the bond moment is low
(d) there is a triple bond between C and O.

12. Which represents alkali metals, based on $(I.E.)_1$ and $(I.E.)_2$ values?

	$(I.E.)_1$	$(I.E.)_2$
(a) X	100	110
(b) Y	95	120
(c) Z	195	500
(d) M	200	250

13. 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) Li < Na < K < Rb (increasing metallic radius)
(c) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ (increasing ionic size)
(d) B < C < N < O (increasing first ionisation enthalpy)
(NEET-I 2016)

14. For AB bond, if percent ionic character is plotted against electronegativity difference $(\chi_A - \chi_B)$, the shape of the curve would look like



The correct curve is
(a) A (b) B (c) C (d) D

15. Electron affinity of the following element is
1. $1s^2, 2s^2, 2p^5$
2. $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
3. $1s^2, 2s^2, 2p^3$
4. $1s^2, 2s^2, 2p^6$
(a) 1 > 2 > 3 > 4 (b) 2 > 1 > 3 > 4
(c) 4 > 3 > 2 > 1 (d) 2 > 3 > 1 > 4

16. The ionic radii (in Å) of N^{3-}, O^{2-} 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)**

17. Which of the following statements are true?
1. PH_5 and $BiCl_5$ do not exist.
2. $p\pi - d\pi$ bond is present in SO_2.
3. I_3^+ has bent geometry.
4. SeF_4 and CH_4 have same shape.
(a) 1, 2, 3 (b) 1, 3
(c) 1, 3, 4 (d) 1, 2, 4

18. Consider the following changes :
$A \rightarrow A^+ + e^-; E_1$ and $A^+ \rightarrow A^{2+} + e^-; E_2$
The energy required to pull out 1st and 2nd electrons are E_1 and E_2 respectively. The correct relationship between two energies would be
(a) $E_1 < E_2$ (b) $E_1 = E_2$
(c) $E_1 > E_2$ (d) $E_1 \geq E_2$

19. Polarising action of Cd^{2+} on anions is stronger than that of Ca^{2+} because
(a) the charges of the ions are same
(b) their radii are same (Ca^{2+} = 0.104 nm; Cd^{2+} = 0.99 nm)
(c) the Ca^{2+} ion has a noble gas electronic configuration, and the Cd^{2+} ion, an 18-electronic configuration of its outer shell
(d) all of the above are correct.

20. AB is predominantly ionic as $A^+ B^-$ if
(a) $(I.E.)_A < (I.E.)_B$ (b) $(I.E.)_A < (E.A.)_B$
(c) $(E.N.)_A < (E.N.)_B$ (d) $(I.E.)_B < (I.E.)_A$

21. sp^3d^2 hybridisation is not displayed by
(a) SF_6 (b) PF_5
(c) $[CrF_6]^{3-}$ (d) BrF_5
(JEE Main 2017 Online)

22. The electron gain enthalpy value (in kJ mol^{-1}) of three halogens, X, Y and Z are respectively −349, −328 and −325. Then X, Y and Z are respectively
(a) F, Cl and Br (b) Cl, F and Br
(c) Cl, Br and F (d) Br, Cl and F

23. In which pair or pairs is the stronger bond found in the first species?
I : O_2^{2-}, O_2; II : N_2, N_2^+; III : NO^+, NO^-
(a) I only (b) II only
(c) I and III only (d) II and III only

24. Out of N_2O, SO_2, I_3^+, I_3^-, H_2O, NO_2^-, and N_3^-, the linear species are
(a) NO_2^-, I_3^+, H_2O (b) N_2O, I_3^+, N_3^-
(c) N_2O, I_3^-, N_3^- (d) N_3^-, I_3^+, SO_2

25. The element $Z = 114$ has been discovered recently. It will belong to which of the following family/group and electronic configuration?
(a) Carbon family, $[Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^2$
(b) Oxygen family, $[Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^4$
(c) Nitrogen family, $[Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^6$
(d) Halogen family, $[Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^5$
(NEET 2017)

26. The molecule may be represented three resonating structure having energies E_1, E_2 and E_3 respectively. The energy follows the order $E_3 > E_2 > E_1$. If the actual energy content of the molecules is (E_0). The resonance energy is
(a) $E_2 - E_0$ (b) $E_1 - E_0$
(c) $(E_1 + E_2 + E_3) - E_0$ (d) $E_3 - E_0$

27. Energy of an electron in the ground state of the hydrogen atom is -218×10^{-18} J. The ionisation enthalpy of atomic hydrogen is
(a) 4.314×10^6 J mol^{-1} (b) 2.52×10^{-6} J mol^{-1}
(c) 1.313×10^6 J mol^{-1} (d) 2.33×10^5 J mol^{-1}

28. Assuming 2*s*-2*p* 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 2017)

29. An elements which belong to 3rd period and 14th group, has electronic configuration
(a) $1s^2, 2s^2, 2p^6, 3s^2$ (b) $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
(c) $1s^2, 2s^2, 2p^6, 3s^2, 3p^3$
(d) $1s^2, 2s^2, 2p^3$

30. Which one of the following compounds shows the presence of intramolecular hydrogen bond?
(a) H_2O_2 (b) HCN
(c) Cellulose
(d) Concentrated acetic acid. **(NEET-II 2016)**

SOLUTIONS

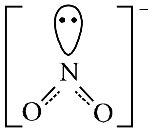
1. **(d):** $AlCl_3$ is covalent in solid or gaseous state. In polar solvents, it becomes ionic due to high heat of hydration ($\because$ Al has high +3 charge) and it exists as $[Al(H_2O)_6]^{3+}$ and Cl^-.

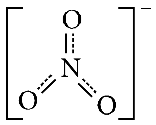
2. **(b):** Stable configuration with all unpaired electron in *f*-orbital is $[Xe]_{54}\ 6s^2 4f^7 5d^1$

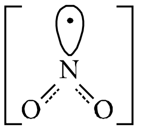
3. **(c):** NH_4^+ : sp^3 hybridisation, 109°28′
$\ddot{N}H_3$: sp^3 hybridisation, 107°48′ due to *bp-lp* repulsion
NH_2^- : sp^3 hybridisation, 104°27′ due to *lp-lp* repulsion
$\therefore$ Order for bond angle is $NH_4^+ > NH_3 > NH_2^-$.

4. **(d):** P^{5+} has more effective nuclear charge and smaller size than P^{3+}.

5. **(a):** $[O=N=O]^+$
sp hybridisation


*sp*² hybridisation


*sp*² hybridisation


*sp*² hybridisation

6. **(d)**

7. **(c):** Since water is polar in nature and like dissolve like, therefore, the coating must be in non-polar to polar manner.

8. **(a):** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$, $Z = 15$ *i.e.,* phosphorus.
Atomic number of element below it = 15 + 18 = 33 *i.e.,* arsenic.

9. **(b)**
1. $lp - lp = 0$; $lp - bp = 4$; $bp - bp = 2$
2. $lp - lp = 1$; $lp - bp = 3$; $bp - bp = 2$
3. $lp - lp = 0$; $lp - bp = 6$; $bp - bp = 0$

Structure (1) is most stable because it has minimum *lp-lp* repulsion as compared to (2) and minimum *lp-bp* repulsion as compared to (3).

10. **(b):**

Ion :	Mn^{2+}	Cu^{2+}	Fe^{2+}	Ni^{2+}
E.C. :	$3d^5$	$3d^9$	$3d^6$	$3d^8$
Number of unpaired electrons :	5	1	4	2

Hence, lowest paramagnetism is shown by $CuSO_4.5H_2O$.

11. **(a):** CO is referred as practically non-polar as it possess very small dipole moment because electron drift from C to O is almost nullified by the π-electron drift from O to C.

12. **(c):** For alkali metals:
$(I.E.)_1 << (I.E.)_2$

13. **(a, d):** 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.

14. **(c):** Ionic character is 50% when electronegativity difference is about 1.9 which is for curve (*C*).

15. **(b):** $1s^2, 2s^2, 2p^5$ (F)
$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$ (Cl)

$1s^2, 2s^2, 2p^3$ (N)
$1s^2, 2s^2, 2p^6$ (Ne)
Electron affinity : Cl > F > N > Ne
Thus, $\underset{2}{\text{Cl}} > \underset{1}{\text{F}} > \underset{3}{\text{N}} > \underset{4}{\text{Ne}}$

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

$$\underset{1.36\ \text{Å}}{F^-} < \underset{1.40\ \text{Å}}{O^{2-}} < \underset{1.71\ \text{Å}}{N^{3-}}$$

17. (a)

18. (a) : Second ionisation energy is always greater than first ionisation energy.

19. (c) **20. (c)**

21. (b) : Hybridisation $(X) = \frac{1}{2}[VE + MA - c + a]$

(a) $SF_6 \Rightarrow X = \frac{1}{2}[6 + 6 - 0 + 0] = 6 \Rightarrow sp^3d^2$

(b) $PF_5 \Rightarrow X = \frac{1}{2}[5 + 5 - 0 + 0] = 5 \Rightarrow sp^3d$

(c) $[CrF_6]^{3-} \Rightarrow sp^3d^2$ hybridisation

(d) $[BrF_5] \Rightarrow X = \frac{1}{2}[7 + 5 + 0 + 0] = 6 \Rightarrow sp^3d^2$

Hence, PF_5 exhibits sp^3d hybridisation, not sp^3d^2.

22. (b) : Electron affinity (or electron gain enthalpy) of halogens follows the order:

$$\begin{array}{lccccc} & \text{Cl} & > & \text{F} & > & \text{Br} \\ \Delta_{eg}H(\text{in kJ mol}^{-1}) & -349 & & -328 & & -325 \end{array}$$

23. (d) : $O_2^{2-} : KK, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$

$\text{B.O.} = \frac{1}{2}(8 - 6) = 1$

$O_2 : KK, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma\, 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^1 = (\pi^* 2p_y)^1$

$\text{B.O.} = \frac{1}{2}(8 - 4) = 2$

Thus, O_2 has stronger bonding than O_2^{2-}.

$N_2 : KK, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^2$

$\text{B.O.} = \frac{1}{2}(8 - 2) = 3$

$N_2^+ : KK, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^1$

$\text{B.O.} = \frac{1}{2}(7 - 2) = 2.5$

Thus, N_2 has stronger bonding than N_2^+.

$NO^+ : KK, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^2$

$\text{B.O.} = \frac{1}{2}(8 - 2) = 3$

$NO^- : KK, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^1 = (\pi^* 2p_y)^1$

$\text{B.O.} = \frac{1}{2}(8 - 4) = 2$

Thus, NO^+ has stronger bonding than NO^-.

24. (c) : $N_2O \Rightarrow \overset{-}{N}{=}\overset{+}{N}{=}O$

$I_3^- \Rightarrow$ with 2 *bp* and 3 *lp* around central atom is linear.
$N_3^- \Rightarrow$ with 2 *bp* (stereoactive pairs) around the central atom is linear.

25. (a) : The electronic configuration of the element with $Z = 114$ (flerovium) is $[Rn]5f^{14}\, 6d^{10} 7s^2 7p^2$.
Hence, it belongs to carbon family which has the same outer electronic configuration.

26. (b) : The energy difference between most stable resonating structure and resonance hybrid structure is known as resonance energy.
Most stable resonating structure will have the minimum energy = E_1
Thus, resonance energy = $E_1 - E_0$.

27. (c) : Energy of the electron in the first orbit of H-atom,

$E_1 = -2.18 \times 10^{-18}$ J

Ionisation energy = $E_\infty - E_n$

Ionisation enthalpy of atomic hydrogen $= (E_\infty - E_1)\, N_A$

$= [0 - (-2.18 \times 10^{-18})] \times 6.023 \times 10^{23}$
$= 2.18 \times 6.023 \times 10^5$ J mol^{-1}
$= 13.13 \times 10^5$ J mol^{-1} $= 1.313 \times 10^6$ J mol^{-1}.

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

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

Applying this configuration, Be_2, B_2 and N_2 will be diagmagnetic, but C_2 will be paramagnetic.

29. (b)

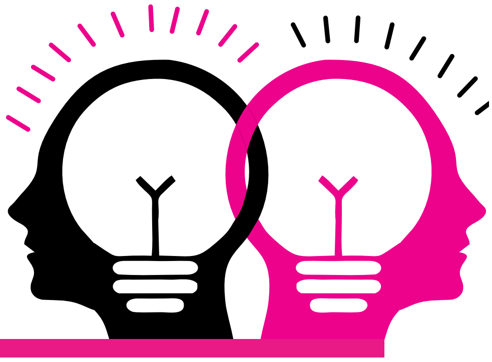
30. (c) : H_2O_2, HCN and conc. CH_3COOH form intermolecular hydrogen bonding while cellulose has intramolecular hydrogen bonding.

◆◆

MPP-4 CLASS XI ANSWER KEY

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

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

1. The Bohr model of the atom described the energy state of electrons with one quantum number. The quantum mechanics model uses how many quantum numbers to describe the energy state of an electron?
(a) One (b) Two (c) Four (d) Ten

2. The velocity of an electron in the second shell of hydrogen atom is
(a) 10.94×10^6 m s^{-1} (b) 18.88×10^6 m s^{-1}
(c) 1.888×10^6 m s^{-1} (d) 1.094×10^6 m s^{-1}

3. In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005%. Certainty with which the position of an electron can be located is ($h = 6.6 \times 10^{-34}$ kg m^{2}s^{-1}; mass of electron, $e_m = 9.1 \times 10^{-31}$ kg)
(a) 1.52×10^{-4} m (b) 5.10×10^{-3} m
(c) 1.92×10^{-3} m (d) 3.84×10^{-3} m

4. If Hund's rule is not followed, magnetic moment of Fe^{2+}, Mn^+ and Cr, all having 24 electrons, will be in order :
(a) $Fe^{2+} < Mn^+ < Cr$ (b) $Fe^{2+} = Cr < Mn^+$
(c) $Fe^{2+} = Mn^+ < Cr$ (d) $Mn^{2+} = Cr < Fe^{2+}$

5. Thomson was convinced that he had discovered a sub-atomic particle, *i.e.*, electron, from the evidence that
(a) the charge-to-mass ratio was the same for all materials
(b) cathode rays could move through vacuum
(c) electrons were attracted toward a negatively charged plate
(d) the charge was always 1.60×10^{-19} coloumb.

6. The orbital angular momentum of a *p*-electron is given as
(a) $\sqrt{3}\dfrac{h}{2\pi}$ (b) $\sqrt{\dfrac{3}{2}\dfrac{h}{\pi}}$ (c) $\sqrt{\dfrac{3h}{\pi}}$ (d) $\dfrac{h}{\sqrt{2}\,\pi}$

7. Which of the following electronic configurations represent the element in the ground state?
(a) $1s^2 2s^1 2p^1$ (b) $1s^2 2s^2 2p^1$
(c) $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$
(d) $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1 3d^1$

8. Which of the following is false?
(a) Pfund spectral series for which $n_1 = 5$ and $n_2 = 6, 7....$ lies in the far infrared region of the electromagnetic spectrum.
(b) Visible region of electromagnetic spectrum has wavelength from 400 nm to 800 nm.

(c) Balmer spectral series lies in the visible portion of the electromagnetic spectrum.
(d) Lyman spectral series lies in the visible portion of the electromagnetic spectrum.

9. Photoelectric emission is observed from a metal surface with incident frequencies ν_1 and ν_2, where $\nu_1 > \nu_2$. If the kinetic energies of the photoelectrons emitted in the two cases are in the ratio 2 : 1, then the threshold frequency ν_0 of the metal is

(a) $\nu_1 - \nu_2$ (b) $\frac{\nu_1 - \nu_2}{h}$
(c) $2\nu_1 - \nu_2$ (d) $2\nu_2 - \nu_1$

10. The major success of the Bohr theory was in explaining
(a) how electrons move in circular orbits
(b) why radiationless orbits existed
(c) the colours in the hydrogen line spectrum
(d) why the angular momentum of the electron should be determined by orbit quantum numbers.

SECTION - II

More than One Options Correct Type

11. Which of the following set of ions have the same number of electrons?

(a) Cr^{3+}, Fe^{2+} (b) Cu^{+}, Zn^{2+}
(c) Mn^{2+}, Fe^{3+} (d) Sc^{3+}, V^{3+}

12. Which of the following statements are correct?
(a) For all values of n, the p orbitals have the same shape but the overall size increases as n increase for a given atom.
(b) The fact that there is a particular direction along which each p-orbital has maximum electron density, plays an important role is determining molecular geometries.
(c) The charge cloud of a single electron in $2p_x$ atomic orbital consists of two lobes of electron density.
(d) Number of radial nodes decreases with increasing value of principal quantum number (n).

13. For which of the following species, the expression for the energy of electron in n^{th} orbit

$$\left(E_n = -\frac{13.6\,Z^2}{n^2}\,\text{eV atom}^{-1}\right)$$ has the validity?

(a) He^{2+} (b) Li^{2+}
(c) Deuterium (d) Tritium

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

A physicist was performing experiments to study the effect of varying voltage on the velocity and wavelength of the electrons. In one case, the electron was accelerated through a potential difference of 1 kV and in the second case, it was accelerated through a potential difference of 2 kV.

14. The velocity acquired by the electron will be
(a) double in the second case than in the first case
(b) four times in the second case than in the first case
(c) same in both cases
(d) 1.4 times in the second case than in the first case.

15. In order to have half the velocity in the second case than in the first case, the potential applied should be
(a) 0.5 kV (b) 2 kV
(c) 0.25 kV (d) 0.75 kV

Paragraph for Questions 16 and 17

When the Schrodinger wave equation was solved for H like ions it gave the following expression for the energy of electron

$$E_n = -\frac{2\pi^2 m_e e^4 Z^2}{n^2 h^2}$$

Substituting the values of various constants for H-atom,

$$E_n = -\frac{1.312\times10^6}{n^2}\ \text{J mol}^{-1}$$

where n is the energy level.

16. Energy associated with second orbit of Li^{2+} is
(a) -2.624×10^6 J mol^{-1} (b) -2.952×10^6 J mol^{-1}
(c) -1.749×10^6 J mol^{-1} (d) -2.09×10^6 J mol^{-1}

17. The wavelength of radiation emitted when an electron in H–atom makes a transition from $n = 2$ to $n = 1$ is
(a) 243.2 nm (b) 121.6 nm
(c) 356.8 nm (d) 82.5 nm

MPP-4 CLASS XII ANSWER KEY

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

SECTION - IV

Matching List Type

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

List I	**List II**
(P) Number of values of l for an energy level	1. 0, 1, 2 ……
(Q) Actual value of l for a particular type of orbital	2. $+l$ …… +2, +1, 0, −1 …… $-l$
(R) Number of m values	3. $(2l + 1)$
(S) Actual values of m for a particular type of orbital	4. n

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

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

List I	**List II**
(P) Photon	1. Value four for N shell
(Q) Electron	2. Probability density
(R) Ψ^2	3. Always positive value
(S) Principle quantum number (n)	4. Exhibits both momentum and wavelength

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

SECTION - V

Assertion Reason Type

20. **Assertion :** For $n = 3$, l may be 0, 1 and 2, and m may be 0, ±1, and 0, ±1, and ±2.

Reason : For each value of n, there are 0 to $(n - 1)$ possible value of l and for each value of l, there are 0 to $\pm l$ value of m.

21. **Assertion :** A spectral line will be seen for a $2p_x - 2p_y$ transition.

Reason : Energy is released in the form of waves of light when the electron drops from $2p_x - 2p_y$ orbital.

22. **Assertion :** For He^+, $3p$ orbital has greater energy than $3s$.

Reason : Energy depends on the azimuthal quantum number.

SECTION - VI

Integer Value Correct Type

23. A 100 watt bulb emits monochromatic light of wavelength 400 nm. If the number of photons emitted by the bulb is $x \times 10^{20}$ per second. Then x is

24. The sum of all the quantum numbers of helium atom is

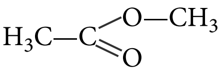
25. The dissociation energy of H_2 is 430.53 kJ mol^{-1}. If hydrogen is dissociated by illumination with radiation of wavelength 253.7 nm, the fraction of the radiant energy which will be converted into kinetic energy approximately is

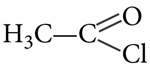
ORGANIC CHEMISTRY-SOME BASIC PRINCIPLES AND TECHNIQUES

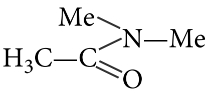
SECTION - I

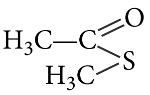
Only One Option Correct Type

1. The least active electrophile is

(a) 
$H_3C{-}C(=O){-}O{-}CH_3$

(b) 
$H_3C{-}C(=O){-}Cl$

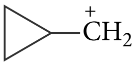
(c) 
$H_3C{-}C(=O){-}N(Me){-}Me$

(d) 
$H_3C{-}C(=O){-}S{-}CH_3$

2. Arrange the following carbocations in decreasing order of stability.

I. $CH_2{=}CH\overset{+}{C}H_2$ II. $CH_2{=}\overset{+}{C}H$

III. $(CH_3)_3\overset{+}{C}$ IV. $Ph_3\overset{+}{C}$

V. 

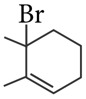
(a) IV > III > I > V > II

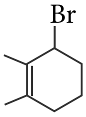
(b) IV > II > III > I > V

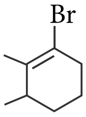
(c) V > IV > I > III > II

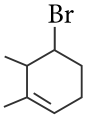
(d) V > IV > III > I > II

3. What is the sum of position assigned to bromine while numbering the parent chain in the given compounds?

I. 

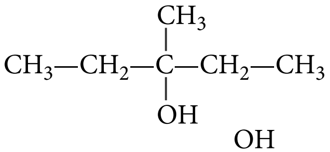
II. 

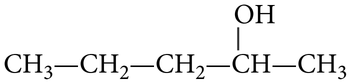
III. 

IV. 

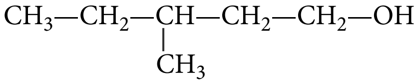
(a) 13 (b) 14 (c) 15 (d) 16

4. Among the following compounds which can be dehydrated very easily ?

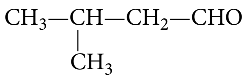
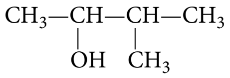
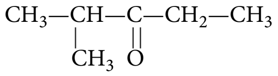
(a) 
$CH_3-CH_2-\underset{OH}{\overset{CH_3}{C}}-CH_2-CH_3$

(b) 
$CH_3-CH_2-CH_2-\overset{OH}{CH}-CH_3$

(c) $CH_3-CH_2-CH_2-CH_2-CH_2-OH$

(d) 
$CH_3-CH_2-\underset{CH_3}{CH}-CH_2-CH_2-OH$

5. Which of the following compounds has wrong IUPAC name?

	Compounds	Name
(a)	$CH_3-CH_2-CH_2-COO-CH_2CH_3$	Ethylbutanoate
(b)	 $CH_3-\underset{CH_3}{CH}-CH_2-CHO$	3-Methyl-butanal
(c)	 $CH_3-\underset{OH}{CH}-\underset{CH_3}{CH}-CH_3$	2-Methyl-3-butanol
(d)	 $CH_3-\underset{CH_3}{CH}-\underset{\overset{\|}{O}}{C}-CH_2-CH_3$	2-Methyl-3-pentanone

6. In an experiment, 0.26 g of an organic compound, in a quantitative analysis, yielded 0.35 g of barium sulphate. The percentage of sulphur in the substance is

(a) 14.5 (b) 16.5 (c) 18.5 (d) 19.5

7. 0.5 g of an organic substance containing phosphorus was heated with conc. HNO_3 in the Carius tube. The phosphoric acid thus formed was precipitated with magnesia mixture ($MgNH_4PO_4$) which on ignition gave a residue of 1.0 g of magnesium pyrophosphate ($Mg_2P_2O_7$). The percentage of phosphorus in the organic compound is

(a) 55.85% (b) 29.72% (c) 19.18% (d) 20.5%

8. 2 g of an organic nitrogen containing compound, on heating, decomposes to give 0.4 g of nitrogen. What should be the formula of the compound?

(a) $C_3H_7N_2Cl$ (b) $C_6H_5N_2Cl$
(c) $(CH_3)_3N$ (d) Data is insufficient

9. 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of an acid required 15 mL of 0.1 M NaOH solution for complete neutralisation. The percentage of nitrogen in the compound is

(a) 29.5 (b) 59.0 (c) 47.4 (d) 23.7

10. Which of the following is not an isomer of butanal?

(a) 2-Butanone (b) 2-Methyl propanal
(c) 2-Butanol (d) But-2-en-1-ol

SECTION - II

More than One Options Correct Type

11. Which of the following statements are correct?

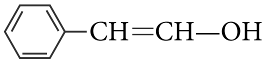
(a) In Lassaigne's test for halogens, conc. HNO_3 is used to remove HCN and H_2S.

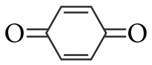
(b) When an organic compound is heated with dry CuO and the gases evolved are passed through lime water which turns milky, the gas may be CO_2 or SO_2.

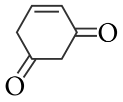
(c) In Carius method, sulphur is oxidised to SO_4^{2-} ion with fuming HNO_3.

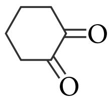
(d) In Lassaigne's test, N present in the organic compound is converted into CN^- ions.

12. Tautomerism is exhibited by

(a) 

(b) 

(c) 

(d) 

13. Resonance structure of a molecule should have

(a) identical arrangement of atoms
(b) nearly the same energy content
(c) same number of paired electrons
(d) identical bonding.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

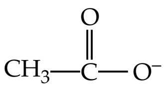
The resonance effect is defined as 'the polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain.

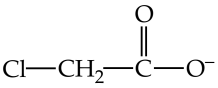
In positive resonance effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. This electron displacement makes certain positions in the molecule of high electron densities.

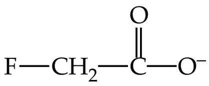
In negative resonance effect, the transfer of electrons is towards the atom or substituent group attached to the conjugated system.

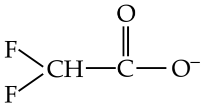
14. Which of the following does not show resonance effect?
(a) 1, 3-Butadiene (b) Acrylonitrile
(c) Nitrobenzene
(d) Isopropyl isothiocyanate

15. Which of the following carboxylate ions is the most stable?

(a) 
$CH_3-\overset{O}{\overset{\|}{C}}-O^-$

(b) 
$Cl-CH_2-\overset{O}{\overset{\|}{C}}-O^-$

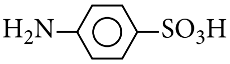
(c) 
$F-CH_2-\overset{O}{\overset{\|}{C}}-O^-$

(d) 

Paragraph for Questions 16 and 17

In Lassaigne test, for the detection of elements in the organic compound, the covalent organic compounds are converted into ionic compounds by fusion with metallic sodium. The nitrogen, sulphur and halogens are converted into cyanides, sulphides and halides respectively which are then detected by their usual chemical tests.

16. Which of the following compounds will respond to Lassaigne test for nitrogen?
(a) NH_2NH_2 (b) $NaCN$
(c) NH_4Cl (d) $NaNO_3$

17. Which of the following will give blood red colour while testing for nitrogen by Lassaigne test?
(a) 

(b) NH_2CONH_2
(c) $C_6H_5SO_3H$ (d) $(NH_4)_2SO_4$

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 codes given below the lists :

	List I (Aromatic compound)		List II (Factor responsible for electrophilic substitution)
(P)	$C_6H_5CH{=}CH_2$	1.	$+E$ effect
(Q)	$C_6H_5CCl_3$	2.	$+M$ effect
(R)	$C_6H_5OCOCH_3$	3.	Hyperconjugation
(S)	C_6H_5OH in presence of NaOH	4.	$-I$ effect

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

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

	List I		List II
(P)	Inductive effect	1.	Delocalisation of σ-electrons with π-bond
(Q)	Resonance	2.	Strong effect
(R)	No bond resonance	3.	Permanent effect
(S)	Electromeric effect	4.	Delocalisation of π-electrons

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

SECTION - V

Assertion Reason Type

20. **Assertion :** Dumas method is more applicable to nitrogen containing organic compounds than Kjeldahl's method.
Reason : Kjeldahl's method does not give satisfactory results for compounds in which N is linked to O atom.

21. **Assertion :** Metamers can also be position or chain isomers.
Reason : Tautomerism was introduced by C.P. Laar to explain the chemical reactivity of a substance according to two possible structures.

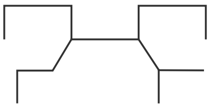
22. **Assertion :** Butane and 2-methylbutane are homologues.
Reason : Butane is a straight chain alkane while 2-methylbutane is a branched chain alkane.

SECTION - VI

Integer Value Correct Type

23. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is

24. How many carbon atoms are present in parent carbon chain in following compound?



25. An alkaloid contains 17.28% of nitrogen and its molecular mass is 162. The number of nitrogen atoms present in one molecule of alkaloid is

SOLUTIONS

STRUCTURE OF ATOM

1. (c)

2. (d): $v_n = 2.188\times10^6 \times \frac{Z}{n} = 2.188\times10^6 \times \frac{1}{2}$

$= 1.094\times10^6$ m s^{-1}

3. (c): $\Delta v = \frac{0.005}{100}\times 600 = 0.03$

$$\Delta x \times m\Delta v = \frac{h}{4\pi} \Rightarrow \Delta x = \frac{6.6\times10^{-34}}{4\times3.14\times9.1\times10^{-31}\times0.03}$$

$= 1.92\times10^{-3}$ m

4. (b): Fe^{2+} : $[Ar]3d^6$; unpaired electron = 0

Mn^+ : $[Ar]3d^5\,4s^1$; unpaired electrons = 2

Cr : $[Ar]3d^4\,4s^2$; unpaired electron = 0

If Hund's rule is not followed.

5. (a)

6. (d): As orbital angular momentum $= \sqrt{l(l+1)}\,\frac{h}{2\pi}$

$$= \sqrt{1(1+1)}\,\frac{h}{2\pi} = \frac{h}{\sqrt{2}\pi}$$

7. (b)

8. (d): Lyman spectral series lies in the ultraviolet region.

9. (d): $h\nu_1 = h\nu_0 + K.E.$ ...(i)

$h\nu_2 = h\nu_0 + \frac{1}{2}K.E.$ or $2h\nu_2 = 2h\nu_0 + K.E.$ ...(ii)

Substracting eqn. (ii) from eqn. (i) gives ;

$h\nu_1 - 2h\nu_2 = h\nu_0 - 2h\nu_0$

or $\nu_1 - 2\nu_2 = -\nu_0$ or $\nu_0 = 2\nu_2 - \nu_1$

10. (c)

11. (b,c) : Number of unpaired electrons : Cr^{3+}(3), Fe^{2+}(4), Cu^+(0), Zn^{2+}(0), Mn^{2+}(5), Fe^{3+}(5), Sc^{3+}(0), V^{3+}(2)

12. (a,b,c)

13. (b,c,d): Li^{2+}, D and T are one electron species. He^{2+} has no electron.

14. (d): Kinetic energy of the electron in case I = 1000 eV

$= 1\times1.602\times10^{-16}$ J $= 1.602\times10^{-16}$ J

Kinetic energy of the electron in case II

$= 2000$ eV$= 2\times1.602\times10^{-16}$ J

$$\therefore \left(\frac{\frac{1}{2}mv_2^2}{\frac{1}{2}mv_1^2}\right) = 2 \quad \text{or} \quad \left(\frac{v_2}{v_1}\right)^2 = 2$$

or $\frac{v_2}{v_1} = \sqrt{2} = 1.4$

15. (c): We want to have $\frac{v_2}{v_1} = \frac{1}{2}$, *i.e.*, $\frac{\frac{1}{2}mv_2^2}{\frac{1}{2}mv_1^2} = \frac{1}{4}$

i.e., $\frac{\text{Potential applied in case II}}{\text{Potential applied in case I}} = \frac{1}{4}$

or potential applied in case II $= \frac{1}{4}\times 1$ kV = 0.25 kV

16. (d): $E_n = \frac{-1.312\times10^6 Z^2}{n^2}$ J mol^{-1}

For second orbit of Li^{2+},

$Z = 3$, $n = 2$

$$E_n = \frac{-1.312\times10^6\times3^2}{2^2} = -2.952\times10^6 \text{ J mol}^{-1}$$

17. (b): $\frac{1}{\lambda} = 109677\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ cm^{-1}

$$\frac{1}{\lambda} = 109677\left(\frac{1}{1^2} - \frac{1}{2^2}\right) \text{cm}^{-1}$$

$$= 109677\left(\frac{1}{1} - \frac{1}{4}\right)\text{cm}^{-1} = 109677\times\frac{3}{4}\ \text{cm}^{-1}$$

$$\lambda = \frac{4}{3}\times\frac{10^7}{109677}\ \text{nm} = 121.6\ \text{nm}$$

18. (b)

19. (a): Photon has particle as well as wave nature. Electron has also particle as well as wave nature. Ψ^2 represents probability density and is always positive. Principle quantum number $n = 4$ for N shell and always has positive value.

20. (a): l(azimuthal quantum number) is always less than n. m_e may have any value equal to l.

21. (d): No spectral line is observed for $2p_x - 2p_y$ transition. No energy is released when electron drops from $2p_x$ to $2p_y$ (because they are degenerate orbitals).

22. (d): In hydrogen and hydrogen like species (one electron species), energy of electron is determined only by principal quantum number, not by n and l. Hence, 3*s* and 3*p* are degenerate orbitals *i.e.*, have equal energies.

23. (2) : Power of the bulb = 100 watt = 100 J s^{-1}

Energy of one photon, $E = h\nu = \dfrac{hc}{\lambda}$

$$= \frac{(6.626\times10^{-34}\ \text{J s})(3\times10^{8}\ \text{m s}^{-1})}{400\times10^{-9}\ \text{m}} = 4.969\times10^{-19}\ \text{J}$$

$$\text{Number of photons emitted} = \frac{100\ \text{J s}^{-1}}{4.969\times10^{-19}\ \text{J}}$$

$$= 2.012\times10^{20}\ \text{s}^{-1}$$

Compairing 2×10^{20} and $x\times10^{20}$, we get $x = 2$.

24. (1) : He : $1s^2$

$n = 1,\ l = 0,\ m = 0 \qquad s = \dfrac{+1}{2}, -\dfrac{1}{2}$

$\text{Sum} = 1+0+0+\dfrac{1}{2}-\dfrac{1}{2}$

25. (9) : Energy of 1 mol of quanta $= h\nu N_A = \dfrac{hcN_A}{\lambda}$

$$= \frac{6.63\times10^{-34}\times3\times10^{8}\times6.023\times10^{23}}{253.7\times10^{-9}} = 472.2\ \text{kJ}$$

Energy converted into kinetic energy

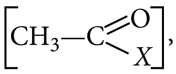
= 472.2 – 430.53 kJ

% of radiant energy converted into kinetic energy

$$= \frac{(472.2-430.53)\times100}{472.2} = 8.82\% \approx 9\%$$

ORGANIC CHEMISTRY-SOME BASIC PRINCIPLES AND TECHNIQUES

1. (c) : In the given electrophiles



$\left[CH_3-C\overset{\displaystyle O}{\underset{\displaystyle X}{\lessgtr}}\right]$,

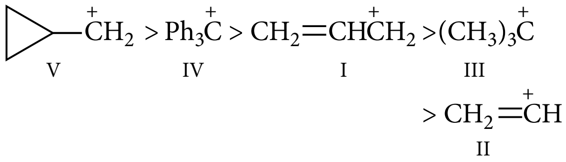
$[CH_3\overset{|}{C}{=}O]$ group is same. So, only *X* affects their activity *i.e.*, we have to discuss activity due to

(a) $-OCH_3$ (b) $-Cl$

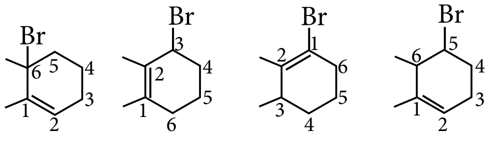
(c) $-N\begin{matrix}\diagup Me\\ \diagdown Me\end{matrix}$ (d) $-S-CH_3$

Since, amines are less active, therefore, electrophile (c) will be least active.

2. (c) : Cyclopropylmethyl carbocation is especially stable because of conjugation between the bent orbitals of the cyclopropyl ring and the vacant *p*-orbital of the cationic carbon. Thus, the decreasing order of stability is



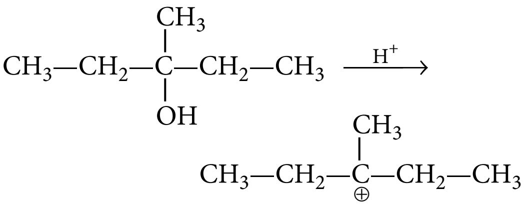
3. (c) :



I II III IV

(6) + (3) + (1) + (5) = 15

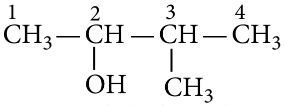
4. (a) :



$$CH_3-CH_2-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-CH_3 \xrightarrow{H^+} CH_3-CH_2-\underset{\oplus}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-CH_2-CH_3$$

The more stable carbocation is generated, thus more easily it will be dehydrated.

5. (c) :



$$\overset{1}{C}H_3-\underset{\displaystyle OH}{\underset{|}{\overset{2}{C}H}}-\underset{\displaystyle CH_3}{\underset{|}{\overset{3}{C}H}}-\overset{4}{C}H_3$$

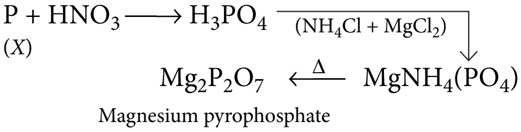
3-Methyl-2-butanol

6. (c) : % of S

$$= \frac{32}{233}\times\frac{\text{Mass of BaSO}_4}{\text{Mass of organic compound}}\times100$$

$$= \frac{32}{233}\times\frac{0.35}{0.26}\times100 = 18.5\%$$

7. (a) :



$$\underset{(X)}{P} + HNO_3 \longrightarrow H_3PO_4 \xrightarrow{(NH_4Cl\,+\,MgCl_2)} MgNH_4(PO_4) \xrightarrow{\Delta} \underset{\text{Magnesium pyrophosphate}}{Mg_2P_2O_7}$$

Molecular weight of $Mg_2P_2O_7$

= 24 × 2 + 31 × 2 + 16 × 7 = 222

$$\text{Percentage of P} = \frac{62}{222}\times\frac{\text{Weight of Mg}_2\text{P}_2\text{O}_7}{\text{Weight of compound}}\times100$$

$$= \frac{62}{222}\times\frac{1.0}{0.5}\times100 = 55.85\%$$

8. (b) : $\underset{2\text{ g}}{\text{N-containing compound}} \xrightarrow{\text{heat}} \underset{0.4\text{ g}}{N_2}$

0.4 g of N_2 is obtained from 2 g of compound

28 g of N_2 is obtained from $\dfrac{2}{0.4}\times28 = 140$

Hence, molecular weight of the compound is 140 which coincides with

$C_6H_5N_2Cl(72 + 5 + 28 + 35.5 = 140.5)$

9. (d): Moles of HCl reacts with ammonia
= Moles of HCl absorbed
– moles of NaOH solution required
$= (20\times0.1\times10^{-3}) - (15\times0.1\times10^{-3}) = 0.5\times10^{-3}$
Thus, moles of NH_3 evolved = 0.5×10^{-3}
= moles of nitrogen in the organic compound
∴ Mass of nitrogen in the organic compound
$= 0.5 \times 10^{-3} \times 14 = 7 \times 10^{-3}$ g
∴ Percentage of nitrogen in the compound

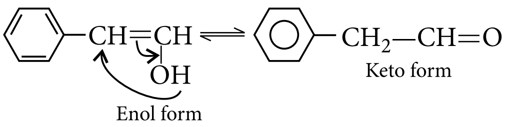
$$= \frac{7\times10^{-3}\times100}{29.5\times10^{-3}} = 23.7\%$$

10. (c)

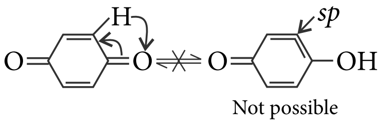
11. (a, b, c, d)

12. (a,c,d) :

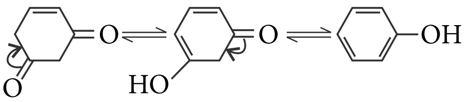
(a)



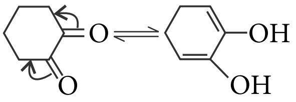
(b)



(c)

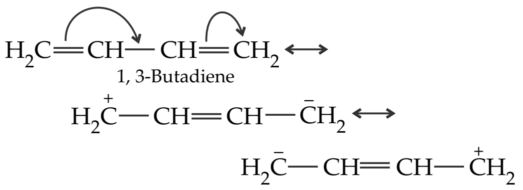


(d)

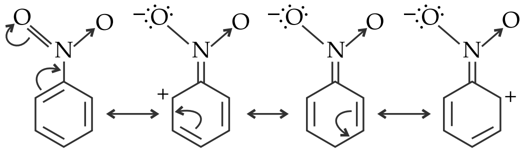


13. (a,b,c)

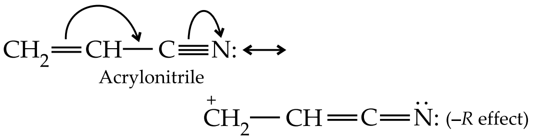
14. (d): Resonance effect involves delocalisation of π-electrons of two or more conjugated double bonds or non-bonding electrons and π-electrons of a double bond.



$H_2C{=}CH{-}CH{=}CH_2 \longleftrightarrow$
1, 3-Butadiene
$H_2\overset{+}{C}{-}CH{=}CH{-}\overset{-}{C}H_2 \longleftrightarrow$
$H_2\overset{-}{C}{-}CH{=}CH{-}\overset{+}{C}H_2$



Nitrobenzene



$CH_2{=}CH{-}C{\equiv}N: \longleftrightarrow$
Acrylonitrile
$\overset{+}{C}H_2{-}CH{=}C{=}\ddot{N}:$ (–*R* effect)

$(CH_3)_2CH - SC{\equiv}N$ does not show resonance effect.
Isopropyl isothiocyanate

15. (d): Stability of carboxylate ion depends on two factors: Electronegativity of the halogen atom and number of halogen atoms attached. More the electronegativity of the halogen atom and more the number of halogen atoms, more will be the dispersal of negative charge.

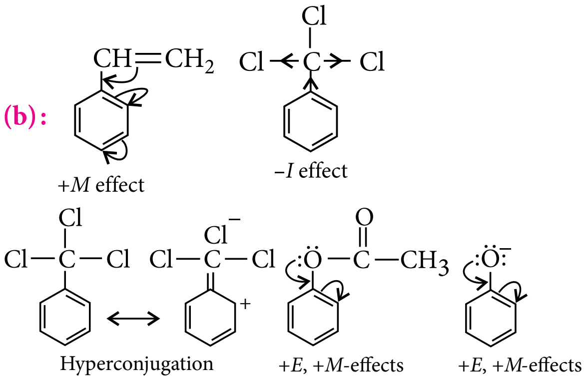
16. (b): Lassaigne test is not given by compounds which do not contain C-atoms but contain N-atoms, because as these compound do not contain C-atoms, so, in sodium extract CN^- ion is not formed.

17. (a): If S is present along with N, blood red colouration is observed.

$Na + C + N + S \longrightarrow NaCNS$

$3NCS^- + Fe^{3+} \longrightarrow Fe(CNS)_3$
Ferric thiocyanate
(Blood-red colour)

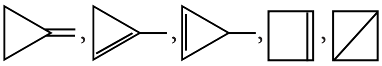
18. (b):



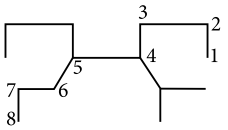
19. (c) **20. (b)**

21. (b) **22. (b)**

23. (5):



24. (8):



25. (2): Mass of nitrogen $= 162 \times \frac{17.38}{100} = 28$

Number of N atoms $= \frac{28}{4} = 2$

◆◆

ACE YOUR WAY CBSE XI

Series 2

CHAPTERWISE PRACTICE PAPER : CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES | CHEMICAL BONDING AND MOLECULAR STRUCTURE

Time Allowed : 3 hours | Maximum Marks : 70

GENERAL INSTRUCTIONS

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

1. What is hybridisation?

2. Arrange the following ions in the order of increasing size :
$Be^{2+}, Cl^{-}, S^{2-}, Na^{+}, Mg^{2+}, Br^{-}$

3. Which of the two is more hard : MgO or CaO ? The internuclear distances of MgO and CaO are 2.05 Å and 2.40 Å respectively.

4. Helium has electronic configuration of $1s^2$ but it is placed in *p*-block in group-18. Explain.

5. How does the concept of formal charge related to the stability of ion or molecule?

6. How does the metallic and non-metallic character vary on moving from left to right in a period?

7. Distinguish between sigma and pi bonds.

8. Account for the following :
- **(a)** Covalent radii are shorter than the metallic radii.
- **(b)** Value of second ionisation enthalpy is greater than the first.

9. Which of the two : peroxide ion or superoxide ion has larger bond length? Explain.

OR

Explain the formation of HCl using valence bond theory.

10. The ionisation enthalpy of sodium is 495 kJ mol^{-1}. Calculate the energy required in joules to convert all atoms of sodium in 2.6 g of sodium vapour into sodium ions.

11. Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds?

12. First member of each group of representative elements (*i.e.*, *s* and *p*-block elements) shows anomalous behaviour. Illustrate with two examples.

13. Calculate the formal charge on each atom in SO_5^{2-} (per-oxosulphate ion).

14. The amount of energy released when 1×10^{10} atoms of chlorine in vapour state are converted to Cl^{-} ions according to the equation,
$Cl_{(g)} + e^{-} \longrightarrow Cl^{-}_{(g)}$ is 57.86×10^{-10} J
Calculate the electron gain enthalpy of chlorine atom in kJ mol^{-1} and eV per atom.

15. Draw Lewis structures for the following molecules and identify the atoms which do not obey octet rule : H_2S, SF_2, BF_3, SO_2, PCl_3, PCl_5

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

OR

Answer the following :

(i) How many elements can be accommodated in the present set up of the long from of periodic table?

(ii) What are superheavy elements?

(iii) What would be IUPAC names and symbols with atomic numbers 126, 134 and 150?

17. Arrange the following sets of molecules in the decreasing order of bond angle :

(i) SF_6, CCl_4, H_2O, NH_3

(ii) CH_4, NH_3, H_2O, BF_3

(iii) $AlCl_3$, H_2S, BeH_2, H_2O

18. (a) What are the atomic numbers and the IUPAC name and symbol for the elements Mendelevium (Md) and Seaborgium (Sg)?

(b) What is the atomic number of the element for which both the American and Soviet scientists claimed credit for the discovery?

(c) Refer to the problem (b) above, what name is given to the above element by the American and Soviet scientists?

(d) Name the metal used as a photoconductor in photocopying machines.

(e) Name and give the atomic number of most poisonous element.

(f) Name the non-metal with highest melting point.

19. (a) In each of the following pairs, select the species having the greater resonance stabilisation.

(i) 
$H_2C{=}O$ and $HC(O^-){=}O$

(ii) HNO_3 and NO_3^-

(b) Draw all possible resonating structures for HN_3.

20. Predict the formulae of the stable binary compounds that would be formed by the following pairs of compounds

(a) Mg and I

(b) Element (X) 113 and F

(c) Element (X) 119 and O.

21. Discuss the structure of XeF_2 using molecular orbital theory. Why do we need MOT explanation of structure?

22. Explain the following :

(i) There are only 14 lanthanides and only 14 actinides.

(ii) Why zero group elements are inert?

(iii) Why Be and Mg atoms do not impart colour in a flame.

23. Sheetal was taught in chemistry class about electron gain enthalpy. In general, the electron gain enthalpy for some third period elements (*e.g.*, P, S, Cl) are more negative than the corresponding second period members (*e.g.*, N, O, F). Sheetal was totally confused and wanted to know the reason for the same. She discussed with her teacher. The teacher explained the phenomenon which satisfied Sheetal.

(i) What would be the answer of the teacher ?

(ii) Which of the following pairs of elements has lesser electron gain enthalpy : N or O?

(iii) Why halogens have highest electron gain enthalpies?

(iv) What values are shown by Sheetal?

24. Deduce the hybridisation, geometry and shape of the following :

(i) CH_2^{2+} **(ii)** Br_3^-

(iii) ClO_3^+ **(iv)** F_2SeO

(v) $IO_2F_2^-$

OR

(i) Explain the following :

(a) Why a molecule is more stable in terms of energy than the uncombined atoms?

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

(c) The density of ice is less than that of water or ice floats over water.

(ii) Methanoic acid, HCOOH, has one carbon-oxygen bond of length 123 pm, and another 136 pm. Which bond has which length?

(iii) Both carbon-oxygen bonds in the methanoate ion, $HCOO^-$, have the same length (127 pm). What does this tell about bonding?

25. Define ionisation enthalpy. Discuss the factors affecting ionisation enthalpy of the elements and its trends in the periodic table.

OR

Write the electronic configuration of the elements given below and also predict the block, group number and period to which they belong. (Z = Atomic number)

(a) Element A ($Z = 5$)
(b) Element B ($Z = 11$)
(c) Element C ($Z = 54$)
(d) Element D ($Z = 59$)
(e) Element E ($Z = 90$)

26. (i) Explain the following :

(a) The dipole moment of NH_3 is more than that of NF_3.

(b) The experimentally determined N—F bond length in NF_3 is greater than the sum of single bond covalent radii of N and F.

(ii) The dipole moment of KCl is 3.336×10^{-29} coulomb metre which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate percentage ionic character of KCl. Also, calculate the dipole moment of KCl molecule, if there were opposite charges of one fundamental unit located at each nucleus.

OR

Arrange the following in the order asked :

(a) Increasing covalent character : NaCl, $MgCl_2$, and $AlCl_3$

(b) Increasing polarising power : Na^+, Ca^{2+}, Mg^{2+} and Al^{3+}

(c) Decreasing dipole moment : CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4

(d) Decreasing ionic nature : MCl, MCl_2 and MCl_3

(e) Increasing dipole moment : H_2O, H_2S, BF_3

SOLUTIONS

1. The intermixing of atomic orbitals of slightly different energies to redistribute their energies and resulting in the formation of new sets of orbitals of equivalent energies and shapes is called hybridisation. The new orbitals are known as hybrid orbitals.

2. $Be^{2+} < Mg^{2+} < Na^+ < Cl^- < S^{2-} < Br^-$

3. MgO, because MgO has less interionic distance than CaO (both have same charges) and, therefore electrostatic force of attraction is more in MgO.

4. Helium has completely filled valence shell, *i.e.*, $1s^2$ like other noble gases and exhibits their properties.

5. The structure which has the smallest formal charge on the atoms is the most stable structure because that structure has the least energy out of all the possible structures.

6. On moving from left to right in a period, the number of electrons increases by one at each succeeding element but the number of shells remain the same. Therefore, the effective nuclear charge increases and consequently the tendency of an atom to lose electron decreases. Hence, metallic character decreases when we move from left to right in a period.

On the other hand, with increase in nuclear charge, the tendency of an atom to gain electron increases. Hence, non-metallic character increases on moving from left to right in a period.

7. Distinguish between sigma and pi bonds :

	Sigma bond (σ)	**Pi bond (π)**
1.	The bond is formed by the overlap of orbitals along their internuclear axes (end to end overlap). It includes *s*-*s* or *p*-*p* or *s*-*p* overlapping.	The bond is formed by sidewise overlapping of orbitals (lateral overlapping). It includes *p*-*p* sidewise overlapping only.
2.	It is a strong bond.	It is a weak bond.
3.	There can be free rotation of atoms around σ-bond.	Free rotation is not possible around π-bond.
4.	The shape of the molecule is determined by σ-bonds.	π-bonds do not affect the shape of the molecule.
5.	σ-electrons are referred to as localized electrons.	π-electrons are referred to as mobile electrons.

8. (a) In a metallic lattice, the valence electrons are mobile, therefore, they are 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, metallic radius is always longer than its covalent radius.

(b) When an electron is removed from the gaseous neutral gaseous atom, the effective nuclear charge increases, thus the value of second ionisation enthalpy increases.

9. The bond length of a molecule is related to its bond order. Larger the bond order, the smaller will be the bond length.

Superoxide ion O_2^- :

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

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{8-5}{2} = 1.5$$

Peroxide ion, O_2^{2-} :

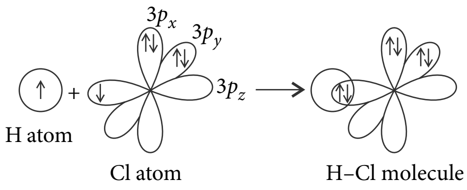
$$KK(\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{8-6}{2} = 1$$

As, superoxide ion (O_2^-) has greater bond order than peroxide ion (O_2^{2-}), therefore, bond length of peroxide ion will be larger.

OR

In HCl molecule, chlorine atom having one unpaired electron in its *p*-orbital comes closer to hydrogen atom which has one electron in its 1*s* orbital, then the two half-filled orbitals overlap (a 1*s* orbital of hydrogen with the 3*p* orbital of chlorine) each other and a chemical bond is formed between the two atoms.



Thus, the formation of HCl molecule takes place.

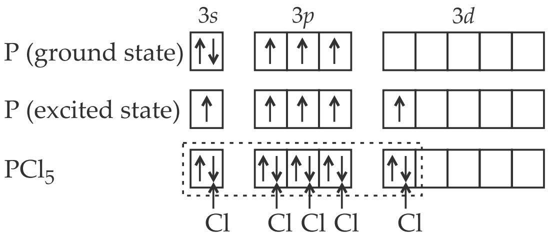
10. Number of moles in 2.6 g of sodium = $\frac{2.6}{23} = 0.113$

Ionisation enthalpy of 1 mole of sodium = 495 kJ

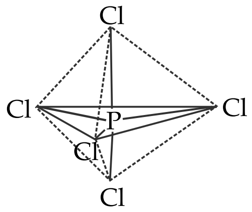
Thus, ionisation enthalpy of 0.113 mole will be

= 495 × 0.113 kJ = 55.935 kJ = 55,935 J

11. Formation of PCl_5 (sp^3d hybridisation) : The ground state and the excited state electronic configurations of phosphorus (Z = 15) are represented as:



sp^3d hybrid orbitals filled by electron pairs donated by five Cl atoms.



Trigonal bipyramidal

All the bond angles in trigonal bipyramidal geometry are not equivalent. Three P–Cl bonds lie in one plane and make angle of 120° with each other, these bonds are termed as equatorial bonds. The remaining two P–Cl bonds, one lying above and below the equatorial plane, make an angle of 90° with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and weaker than the equatorial bonds.

12. First member of each group of *s* and *p*-block elements shows anomalous behaviour due to the following reasons :

i. Small size
ii. High ionisation enthalpy
iii. High electronegativity
iv. Absence of *d*-orbitals

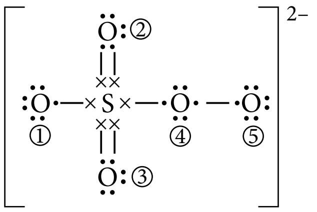
Examples : Li shows different properties from the rest of the first group elements. *e.g.*, covalent nature of its compounds, formation of nitrides.

Similarly, beryllium, the first element of second group differs from its own group in the following ways :

(i) Beryllium carbide reacts with water to produce methane gas while carbides of other elements give acetylene .

(ii) Beryllium shows a coordination number of four while other elements show a coordination number of six.

13. Lewis structure of SO_5^{2-} ion is



Formal charge = [Number of valence electrons] – [Number of lone pair electrons] – ½[Number of bond pair electrons]

(a) Formal charge on S-atom :

Number of valence e^- on S-atom = $6e^-$

Lone pair (lp) electrons on S-atom = 0

Number of bond pair electrons = $6 \times 2 = 12e^-$

$\therefore$ Formal charge $= 6 - 0 - \frac{1}{2} \times (12) = 0$

(b) Formal charge on O-atom (marked 1 and 5) :

Number of valence e^- on O-atom = $6e^-$

Lone pair electrons on O-atom = $3 \times 2 = 6e^-$

Number of bond pair electrons on O-atom = $2e^-$

$\therefore$ Formal charge $= 6 - 6 - \frac{1}{2} \times 2 = -1$ (on each)

(c) Formal charge on O-atom (marked 2 and 3) :

Number of valence e^- on O-atom = $6e^-$

Lone pair electrons on O-atom = $2 \times 2 = 4e^-$

Number of bond pair electrons = $2 \times 2 = 4e^-$

Formal charge

$= 6 - 4 - \frac{1}{2} \times 4 = 0$

(d) Formal charge on O-atom (marked 4) :

Number of valence e^- on O-atom = $6e^-$

Lone pair electrons on O-atom = $2 \times 2e^- = 4e^-$

Number of bond pair electrons = $2 \times 2e^- = 4e^-$

$\therefore$ Formal charge $= 6 - 4 - \frac{1}{2} \times 4 = 0$

Therefore, sum of Formal charges = 0 – 2 + 0 + 0 = –2

Net charge on SO_5^{2-} = – 2

Hence, sum of Formal charge = net charge on the ion.

14. The electron gain enthalpy of chlorine, *i.e.*, the amount of energy released when 1 mole (6.023×10^{23} atom) of chlorine are converted into Cl^- ions will be

$$= -\frac{57.86\times10^{-10}}{1\times10^{10}}\times6.023\times10^{23}$$

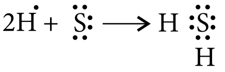
$= -348.49\times10^{3}$ J mol^{-1} = – 348.49 kJ mol^{-1}

Now, 1 eV/atom = 96.49 kJ mol^{-1}

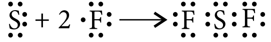
$\therefore$ Electron gain enthalpy of chlorine

$$= -\frac{348.49}{96.49} = -3.61 \text{ eV/atom}$$

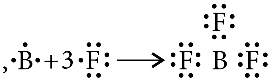
15. The Lewis structures for the molecules are written on the basis of number of electrons in the valence shell of the central atom and shared electron pairs with the other atoms as shown below :

In H_2S,


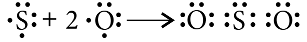
Two H-atoms do not obey octet rule.

In SF_2,


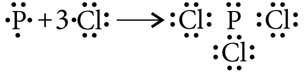
All atoms obey octet rule.

In BF_3,


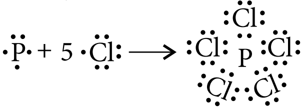
Boron does not obey octet rule.

In SO_2,


S-atom does not obey octet rule.

In PCl_3,


All atoms obey octet rule.

In PCl_5,


P-atoms does not obey octet rule.

16. 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, Ti(22) : $3d^2 4s^2$ can show three oxidation states (+2, +3 and +4) in various compounds like $TiO_2(+4)$, $Ti_2O_3(+3)$ and $TiO(+2)$.

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 electrons to achieve stable configuration while higher oxidation states are achieved by unpairing the paired orbitals and shifting the electrons to vacant d-orbital. *e.g.*,

Phosphorus atom (15) :

Ground state


+3 oxidation state

Excited state


+5 oxidation state

OR

(i) There are seven periods in the present long from of periodic table. In the last period 7*s*, 5*f*, 6*d* and 7*p* orbitals are to be filled, *i.e.*, it can accommodate 32 electrons corresponding to 32 elements. Upto the end of sixth period 86 elements have been accommodated. Thus, the present long form of periodic table can accommodate 86 + 32 = 118 elements.

(ii) Elements with atomic number higher than 92 and decay to lighter nuclei, are called superheavy elements.

(iii) The names and symbols of the elements with atomic numbers 126, 134 and 150 are

Atomic Number	Names	Symbol
126	Unbihexium	Ubh
134	Untriquadium	Utq
150	Unpentnilium	Upn

17. **(i)** CCl_4 > NH_3 > H_2O > SF_6
(109.5°) (107°) (104.5°) (90°)

(ii) BF_3 > CH_4 > NH_3 > H_2O
(120°) (109.5°) (107°) (104.5°)

(iii) BeH_2 > $AlCl_3$ > H_2O > H_2S
(180°) (120°) (104.5°) (100°)

18. **(a)** Atomic number for Mendelevium is 101. Its IUPAC name and symbol is Unnilunium (Unu).
Atomic number for Seaborgium is 106. Its IUPAC name and symbol is Unnilhexium (Unh).

(b) Atomic number is 104.

(c) The American scientist called it Rutherfordium (Rf) and the Soviet scientist called it Kurchatovium.

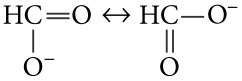
(d) Selenium (Se)

(e) Plutonium (Atomic number 94)

(f) Carbon (Melting point 1400 °C)

19. (a)

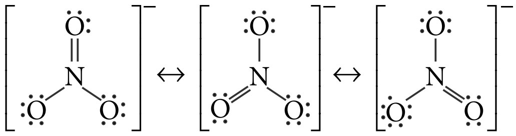
(i) $\underset{\underset{O^-}{|}}{HC}{=}O$ has two equal resonance forms, as shown :



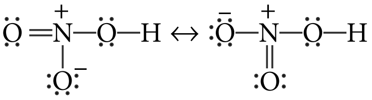
$$\underset{\underset{O^-}{|}}{HC}{=}O \leftrightarrow \underset{\underset{O}{\|}}{HC}{-}O^-$$

$H_2C{=}O$ does not have resonance forms. Hence, it is lower in energy. Thus, $\underset{\underset{O^-}{|}}{HC}{=}O$ is more resonance stabilised.

(ii) NO_3^- has three resonating structure of equal energy as shown:



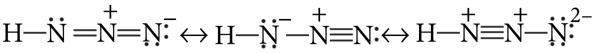
HNO_3 has only two, since the O-atom bonded to the H-atom is not equivalent to the others.



$$O{=}\overset{+}{\underset{\underset{O^-}{|}}{N}}{-}O{-}H \leftrightarrow \overset{-}{O}{-}\overset{+}{\underset{\underset{O}{\|}}{N}}{-}O{-}H$$

Hence, NO_3^- is more resonance stabilized than HNO_3.

(b) The possible structure are shown as :



20. **(a)** Mg is an element of group-2, with $2e^-$ in its valence shell. Therefore, its valency = 2
I is an element of group-17, with > $4e^-$ in its valence shell. Therefore, its valencey = 8 – 7 = 1
∴ Formula = MgI_2

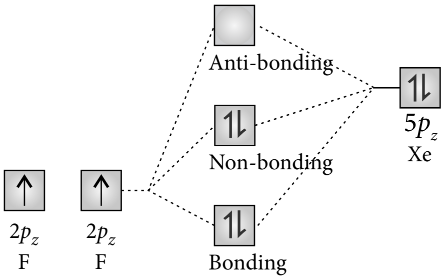
(b) Element (*X*) (At. number = 113) lies in group 13 and 7th period. Hence, its outer shell electronic configuration is $7s^27p^1$, therefore, its valency = 3.
F belongs to group-17 with $7e^-$ in its valence shell. Therefore, its valency = 8 – 7 = 1.
∴ Formula = XF_3.

(c) Element (*X*) (At. number = 119) will be in group-1 and 8th period. Hence, its outer shell electronic configuration is $8s^1$. Therefore, its valency = 1
O is an element of group-16 with $6e^-$ in its valence shell.
Therefore, its valency = 8 – 6 = 2
∴ Formula = X_2O

21. There are two main objections on VB structure of XeF_2.

(i) Size of 5*d*-orbital is too large for effective overlapping.

(ii) In hybridisation, only orbitals of almost same energy take part and 5*p* and 5*d* of Xe differ by ≈ 960 kJ mol^{-1}, then in sp^3d-hybridisation, contribution of more energetic 5*d*-orbital is objectionable. To remove these objections one way is M.O. explanation of the structure.



Assume that bonding involves the $5p_z$ orbital of Xe and $2p_z$ orbitals of two F-atoms. For bonding to occur, orbitals with same symmetry must overlap. These three atomic orbitals combine to give 3MO, one bonding, one non-bonding and one antibonding.

Energy of bonding M.O. < Non-bonding M.O. < Anti-bonding M.O. Linear combination of atomic orbitals and filling of four electrons in these molecular orbitals is represented in the diagram. The four electrons occupy bonding and non-bonding M.O.

22. **(i)** In lanthanides and actinides, the differentiating electron enters to $(n - 2)$ f-subshell. The maximum capacity of f-subshell is of 14 electrons. Thus, there are only 14 lanthanide ($4f^{1-14}$) and 14 actinide ($5f^{1-14}$) elements.

(ii) Zero group elements are inert because they have completely filled outermost shells. Neither they have a tendency to lose or gain or share electrons with other elements.

(iii) Be and Mg atoms are comparatively smaller and their ionisation energies are very high. Hence, their electrons are not excited by the energy of the flame to higher energy state. Therefore, these elements do not give any colour in flame.

23. **(i)** Due to small size of the atoms of nitrogen, oxygen and fluorine, there is a strong inter-electronic repulsion when extra electron is added to these atoms, *i.e.*, electron density is high and the addition of electron is not easy. Thus, the electron gain enthalpies of third period elements, phosphorus, sulphur and chlorine, have more negative values than corresponding elements nitrogen, oxygen and fluorine of second period.

(ii) N has lesser electron gain enthalpy due to stable half-filled electronic configuration.

(iii) (a) Small atomic size and high nuclear charge of halogens in a period.

(b) Halogens have the general electronic configuration of ns^2np^5, *i.e.*, one electron less than stable noble gas (ns^2np^6) configuration.

Thus, halogens have a very strong tendency to accept an additional electron and their electron gain enthalpies are, therefore, high.

(iv) Values shown by sheetal are curiosity, seriousness about her studies.

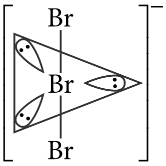
24. **(i)** CH_2^{2+}:

$$H = \frac{1}{2}\ (V + M - \text{number of +ve charge})$$

$$\frac{1}{2}\ (4 + 2 - 2) = 2 = sp \text{ hybridisation}$$

Geometry and shape are linear.

(ii) $Br_3^-: \left[:\ddot{\underset{\cdot\cdot}{Br}}-\ddot{\underset{\cdot\cdot}{Br}}-\ddot{\underset{\cdot\cdot}{Br}}:\right]^-$



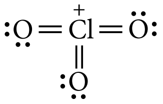
$$H=\frac{1}{2}(V+M+\text{number of –ve charge})$$

$$= \frac{1}{2}\ (7 + 2 + 1)$$

$$= 5 = sp^3d \text{ hybridisation}$$

Br_3^- has trigonal bipyramidal geometry but due to the presence of three lone pairs of electrons, it is linear in shape.

(iii) ClO_3^+ :



$$:\underset{\cdot\cdot}{O}=\overset{+}{Cl}=\ddot{O}: \quad (Cl=\ :\underset{\cdot\cdot}{O})$$

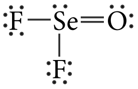
$$H = \frac{1}{2}\ (V + M - \text{number of +ve charge})$$

$$= \frac{1}{2}\ (7 + 0 - 1) = 3$$

$$= sp^2 \text{ hybridisation} = \text{Trigonal planar}$$

ClO_3^+ is unstable ion.

(iv) F_2SeO :

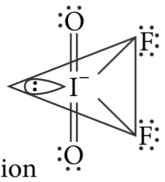


$$:\ddot{\underset{\cdot\cdot}{F}}-\ddot{Se}=\ddot{O}: \quad (Se-\ :\ddot{\underset{\cdot\cdot}{F}}:)$$

$$H = \frac{1}{2}\ (V + M) = \frac{1}{2}\ (6 + 2) = 4 = sp^3 = \text{Tetrahedral}$$

F_2SeO has tetrahedral geometry but due to the presence of one lone pair of electrons, it is pyramidal in shape. This structure is analogous to SO_3^{2-}.

(v) $IO_2F_2^-$:



$H = \frac{1}{2}$(V + M + number of – ve charge)

$= \frac{1}{2}(7 + 2 + 1) = 5 = sp^3d$ hybridisation

It has sp^3d hybridisation with trigonal bipyramidal geometry but due to the presence of one *lp* of e^-, it has see-saw shape.

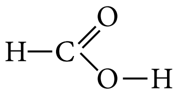
OR

(i) (a) When the atoms combine together to form a molecule energy is always released. Thus, potential energy of a molecule is less than that of uncombined atoms and therefore, the molecule is more stable.

(b) Oxygen has high electronegativity than sulphur. As a result, H_2O forms hydrogen bonding, whereas, there is no hydrogen bonding in H_2S. Consequently, the molecules of water come nearer to each other through hydrogen bonding. This results in higher boiling point of water and hence it is a liquid.

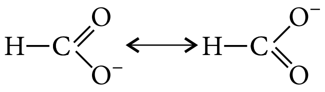
(c) In ice, water molecule is associated with four other molecules through hydrogen bonding in a tetrahedral manner, *i.e.,* it has an open-cage like structure in which lesser molecules are packed per mL. When ice melts, the molecules come close to one another. Consequently, the density of water in liquid state is more than in solid state. Thus, ice floats over water.

(ii) The structure of the methanoic acid is :

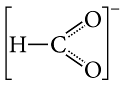


The double bonding carbon-oxygen bond is shorter than the other. A double bond between two atoms is always stronger and shorter than a single bond between the same atoms.

(iii) This is due to the presence of resonance in the molecule.



Each bond has part of the character of single bond and part of character of a double bond. The electrons are delocalized over the three atoms.



Thus, the resonance hybrid has equal bond length and bond order of both C—O bonds.

25. Ionisation enthalpy : It is the energy required to remove an electron from an isolated gaseous atom in its ground state.

$$X_{(g)} \longrightarrow X_{(g)}^+ + e^-$$

Factors affecting ionisation enthalpy :

(i) Effective nuclear charge or the attraction of electrons towards the nucleus : The ionisation energy increases with increase in nuclear charge. The valence electrons are held tightly by the nucleus with increase in nuclear charge, and therefore, greater energy is required to remove valence electrons.

(ii) Penetration power of orbitals : The penetration power of *s*, *p*, *d* and *f* orbitals is in the order $s > p > d > f$. Hence, it is easier to remove an electron from 2*p* orbital as compared to 2*s* orbital. *e.g.*, I.E. of B < I.E. of Be.

(iii) Symmetry of the orbital : Half-filled and fully filled orbitals have extra stability hence, the atoms with half-filled or fully filled orbitals have higher ionisation enthalpy. *e.g.*, *I.E.* of N > *I.E.* of O.

(iv) Atomic size : With increase in atomic size, the ionisation enthapy decreases as the attractive force on the valence electrons decreases.

Trend in the periodic table : Ionisation enthalpy increases along a period from left to right and decreases down the group.

OR

(a) Element *A* ($Z = 5$) : Name of element = Boron (B)

Electronic configuration of $A = 1s^2\,2s^2\,2p^1$

The last electron enters in 2*p* orbital, therefore, it belongs to *p*-block.

Group number = 10 + number of electrons in the valence shell = 10 + 3 = 13

Period of the element = Number of the principal quantum number of the valence shell = 2nd

(b) Element *B* ($Z = 11$) : Name of element = Sodium (Na)

Electronic configuration of $B = 1s^2\,2s^2\,2p^6\,3s^1$

The last electron enters in 3*s*-orbital, therefore, it belongs to *s*-block.

Group number = Number of electrons in the valence shell = 1

Period of the element = Number of the principal quantum number of valence shell = 3rd

(c) Element *C* ($Z = 54$) : Name of element = Xenon (Xe)

Electronic configuration : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2\,5p^6$

The last electron enters in 5*p*-orbital, therefore, it belongs to *p*-block.

Group number = 10 + Number of electrons in the valence shell = 10 + 8 = 18

Period of the element = Number of the principal quantum number of the valence shell = 5th

(d) Element *D* ($Z = 59$) : Name of element = Praseodymium (Pr)

Electronic configuration : = [Xe] $4f^3\ 6s^2$

The last electron enters into the 4*f*-orbital, therefore, it belongs to *f*-block.

Group Number : Since it belongs to the lanthanide series, therefore as such it does not have any group number of its own but it is considered to lie in group-3.

Period of the element : Number of principal quantum number of the valence shell = 6th.

(e) Element *E* ($Z = 90$) : Name of element = Thorium (Th)

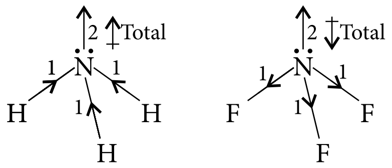
Electronic configuration of *E* : [Rn] $6d^2\ 7s^2$

It belongs to *f*-block elements.

Group number : Since it belongs to actinide series therefore as such it does not have any group number of its own but it is considered to lie in group-3.

Period of the element = Number of the principal quantum number of the valence shell = 7th.

26. (i) (a) In NH_3, the dipole moment due to lone pair of electrons is in the same direction as the resultant dipole moment of the N – H bonds whereas, in case of NF_3, the dipole due to lone pair and the resultant N – F bond moments are in opposite directions. Thus, NF_3 has low dipole moment than NH_3.



(b) The experimentally determined N – F bond length in NF_3 is greater than the sum of single bond covalent radii of N and F. This is due to the partial ionic character of the bonds between unlike atoms and the difference is very much marked in the case of the most strongly electronegative elements F, O and N.

(ii) Dipole moment, $\mu = q \times d$

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

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

For 1.602×10^{-19} charge on each end of dipole, % ionic character = 100

∴ For 1.283×10^{-19} charge on each end of dipole, % ionic character

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

If one unit charge, then

$q = 1.602 \times 10^{-19}$ C

$\therefore \quad \mu = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10}$

$= 4.1652 \times 10^{-29}$ coulomb metre

OR

(a) Smaller cation have greater polarising power. Hence, form more covalent compounds.

$NaCl < MgCl_2 < AlCl_3$

(b) Smaller the size of cation, greater is its polarising power.

$Na^+ < Ca^{2+} < Mg^{2+} < Al^{3+}$

(c) $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

(d) $MCl > MCl_2 > MCl_3$

(e) $BF_3 < H_2S < H_2O$

◆

MPP-4 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.

States of Matter | Thermodynamics

Total Marks : 120 **Time Taken : 60 Min.**

NEET / AIIMS

Only One Option Correct Type

1. The ratio of average speed of an oxygen molecule to the root mean square speed of a nitrogen molecule at the same temperature is

(a) $\left(\frac{3\pi}{7}\right)^{1/2}$ (b) $\left(\frac{7}{3\pi}\right)^{1/2}$

(c) $\left(\frac{3}{7\pi}\right)^{1/2}$ (d) $\left(\frac{7\pi}{3}\right)^{1/2}$

2. The standard enthalpy of formation of NH_3 is -46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1}, the average bond enthalpy of N–H bond in NH_3 will be

(a) -1102 kJ mol^{-1} (b) -964 kJ mol^{-1}

(c) $+352$ kJ mol^{-1} (d) $+1056$ kJ mol^{-1}

3. At 100 °C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, then the volume occupied by water molecules in 1 litre of steam at that temperature is

(a) 6 cm^3 (b) 60 cm^3

(c) 0.6 cm^3 (d) 0.06 cm^3

4. The standard heat of combustion of Al is -837.8 kJ mol^{-1} at 25 °C. If Al reacts with O_2 at 25 °C, which of the following will release 250 kJ of heat?

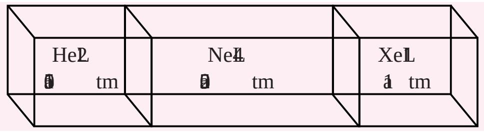
(a) The reaction of 0.624 mol of Al

(b) The formation of 0.624 mol of Al_2O_3

(c) The reaction of 0.312 mol of Al

(d) The formation of 0.150 mol of Al_2O_3

5. Consider the composite system, which is held at 300 K, shown in below figure. Assuming ideal gas behaviour, calculate the total pressure if the barriers separating the compartments are removed. Assuming that the volume of the barriers is negligible. (Given: $R = 0.082$ L atm mol^{-1} K^{-1})



(a) 1 atm (b) 2 atm

(c) 2.3 atm (d) 3.2 atm

6. For the change, $C_{diamond} \longrightarrow C_{graphite}$; $\Delta H = -1.89$ kJ, if 6 g of diamond and 6 g of graphite are separately burnt to yield CO_2, the heat liberated in first case is

(a) more than that in the second case by 1.89 kJ

(b) less than that in the second case by 11.34 kJ

(c) more than that in the second case by 11.34 kJ

(d) more than that in the second case by 0.945 kJ.

7. According to Graham's law, at given temperature the ratio of the rates of diffusion r_A/r_B for gases A and B is

(a) $(p_A/p_B)\,(M_A/M_B)^{1/2}$

(b) $(M_A/M_B)\,(p_A/p_B)^{1/2}$

(c) $(p_A/p_B)\,(M_B/M_A)^{1/2}$

(d) $(M_B/M_A)\,(p_A/p_B)^{1/2}$

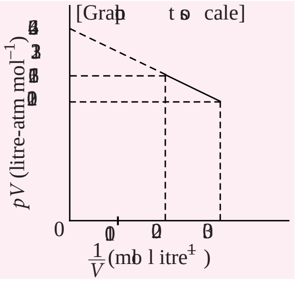
8. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.

(a) $q = 0, \Delta T \neq 0, w = 0$
(b) $q \neq 0, \Delta T = 0, w = 0$
(c) $q = 0, \Delta T = 0, w = 0$
(d) $q = 0, \Delta T < 0, w \neq 0$

9. 'a' and 'b' are van der Waals constants for gases. Chlorine is more easily liquefied than ethane because
(a) a and b for $Cl_2 >$ a and b for C_2H_6
(b) a and b for $Cl_2 <$ a and b for C_2H_6
(c) a for $Cl_2 <$ a for C_2H_6 but b for $Cl_2 >$ b for C_2H_6
(d) a for $Cl_2 >$ a for C_2H_6 but b for $Cl_2 <$ b for C_2H_6

10. The incorrect expression among the following is
(a) in isothermal process, $w_{\text{reversible}} = -nRT \ln \dfrac{V_f}{V_i}$
(b) $\ln K = \dfrac{\Delta H^\circ - T\Delta S^\circ}{RT}$
(c) $K = e^{-\Delta G^\circ/RT}$
(d) $\dfrac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$

11. For one mole of a van der Waal gas when $b = 0$ and $T = 300$ K, the pV vs $1/V$ plot is shown below. The value of the van der Waals constant a (in atm litre^{-2} mol^{-2}) is



(a) 1.0 (b) 4.5 (c) 1.5 (d) 3.0

12. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litre. The change in energy for this process is ($R = 2$ cal mol^{-1} K^{-1})
(a) 163.7 cal (b) 850.2 cal
(c) 1381.1 cal (d) zero.

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 :** Under similar conditions of temperature and pressure, O_2 diffuses 1.4 times faster than SO_2.
Reason : Density of SO_2 is 1.4 times greater than that of O_2.

14. **Assertion :** A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.
Reason : All exothermic reactions are accompanied by decrease of randomness.

15. **Assertion :** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
Reason : The volume occupied by the molecules of an ideal gas is zero.

JEE MAIN / JEE ADVANCED

Only One Option Correct Type

16. A quantity of hydrogen gas occupies a volume of 30.0 mL at a certain temperature and pressure. If temperature is tripled and pressure is reduced to one-ninth of the original value, then half of the mass of hydrogen gas will occupy the volume
(a) 270 mL (b) 90 mL
(c) 405 mL (d) 137 mL

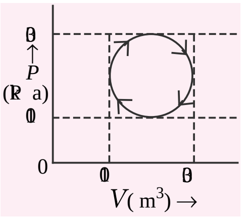
17. The heat of atomisation of PH_3 (g) is 228 kcal mol^{-1} and that of P_2H_4 (g) is 355 kcal mol^{-1}. The energy of the P — P bond will be
(a) 102 kcal mol^{-1} (b) 51 kcal mol^{-1}
(c) 26 kcal mol^{-1} (d) 204 kcal mol^{-1}

18. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is
(Given : $\Delta_r H^\circ_{298K} = -54.07$ kJ mol^{-1},
$\Delta_r S^\circ_{298K} = 10$ J K^{-1} mol^{-1} and $R = 8.314$ J K^{-1}mol^{-1})
(a) 5 (b) 10 (c) 95 (d) 100

19. The pressure-volume work for an ideal gas can be calculated by using the expression $w = -\int_{V_i}^{V_f} p_{ex} dV$.
The work can also be calculated from pV–plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume V_i to V_f, choose the correct option.
(a) w (reversible) = w (irreversible)
(b) w (reversible) < w (irreversible)
(c) w (reversible) > w (irreversible)
(d) w (reversible) = w (irreversible) + $p_{ex} \Delta V$

More than One Options Correct Type

20. Which of the following are not correct for a cyclic process as shown in the figure?



(a) $dU = 0$
(b) $q = -w$
(c) $w = 314$ J
(d) $w = 31.4$ J

21. A 5 L flask containing 1.0 g of hydrogen is heated from 300 K to 600 K. Which of the following statements are correct?
(a) The pressure of the gas is increased.
(b) The rate of collision is increased.
(c) The energy of the gaseous molecules is increased.
(d) The number of the moles of the gas is increased.

22. Among the following, the state functions are
(a) internal energy
(b) irreversible expansion work
(c) reversible expansion work
(d) molar enthalpy.

23. Which of the following statements are correct?
(a) At constant temperature, the gas density is directly proportional to pressure.
(b) At higher pressures, gases deviate from Boyle's law.
(c) Plots of p *vs* T at constant volumes for an ideal gas are parabolic.
(d) At –273 K, gases have zero volume which corresponds to solid state.

Integer Answer Type

24. $\Delta_f H°$ of hypothetical MgCl is -125 kJ mol^{-1} and for $MgCl_2$ is -642 kJ mol^{-1}. The enthalpy of disproportionation of MgCl is $-49\,x$. What will be the value of x?

25. At identical temperature and pressure, the rate of diffusion of hydrogen gas is $3\sqrt{3}$ times that of a hydrocarbon having molecular formula C_nH_{2n-2}. What is the value of n?

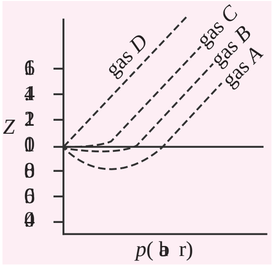
26. A gas expands against a constant external pressure so that the work done is 607.8 J. The work done in litre atmosphere is

Comprehension Type

The real gases show deviations from ideal behaviour. It is observed that real gases do not follow Boyle's law, Charle's law and Avogadro's law perfectly under all conditions.

The deviations from ideal behaviour can be measured in terms of compressibility factor, Z, which may be defined as :

$$Z = \frac{pV}{nRT}$$



It has been observed that Z has values greater than and less than one for different real gases. The behaviour of some common gases is shown in the graph.

27. The gas which is more compressible at low pressure and less compressible at high pressures than expected from ideal behaviour is
(a) A
(b) B
(c) D
(d) both A and B

28. For one mole of gas D, the van der Waals equation reduces to the form
(a) $pV = RT - \frac{a}{V}$
(b) $pV = RT$
(c) $pV = RT + pb$
(d) $pV = RT - pb$

Matrix Match Type

29. Match the transformation in Column I with appropriate options in Column II and choose the correct option.

Column I	**Column II**
(A) $\left(\frac{\partial U}{\partial V}\right)_T = 0$	(p) Isothermal process
(B) $w = -\Delta U$	(q) $-nFE°$
(C) $\Delta U = 0$	(r) Adiabatic process
(D) $\Delta G°$	(s) van der Waals gas
(E) $\left(\frac{\partial T}{\partial P}\right)_H \neq 0$	(t) Ideal gas

(a) A-p, B-q, C-s, D-r, E-t
(b) A-p, B-r, C-t, D-q, E-s
(c) A-t, B-p, C-r, D-q, E-s
(d) A-t, B-r, C-p, D-q, E-s

30. Match the Column I (composition of a gaseous mixture) with Column II (partial pressure exerted) and choose the correct option.

Column I	**Column II**
(A) Hydrogen gas ($p = 200$ atm, $T = 273$ K)	(p) Compressibility factor $\neq 1$
(B) Hydrogen gas ($p \approx 0$ atm, $T = 273$ K)	(q) Attractive forces are dominant
(C) CO_2 ($p = 1$ atm, $T = 273$ K)	(r) $pV = nRT$
(D) Real gas with very large molar volume	(s) $p(V - nb) = nRT$

(a) A-p,r B-q, C-p, D-s
(b) A-p,s, B-r, C-p,q, D-s
(c) A-p,s, B-r, C-p,q, D-r
(d) A-p,r, B-s, C-p,q, D-r

◇◇

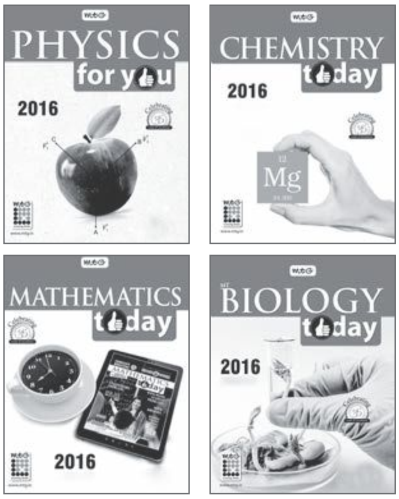
Keys are published in this issue. Search now! ☺

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.



NEET | JEE ESSENTIALS

Class XII

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

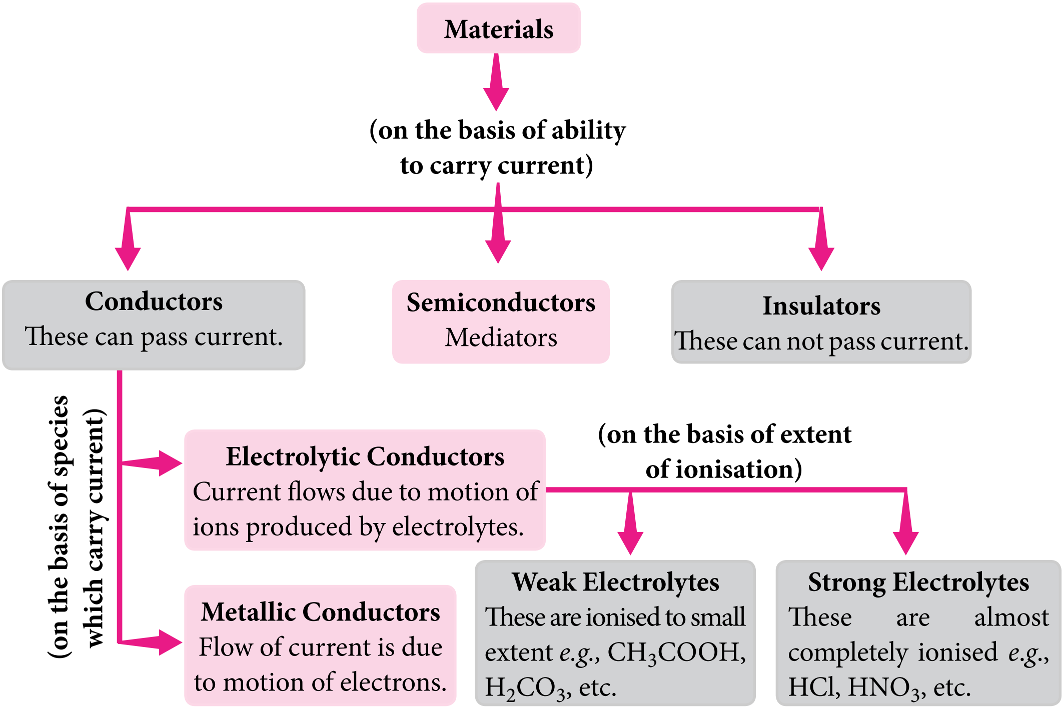
Unit 2

Electrochemistry | Chemical Kinetics | Surface Chemistry

ELECTROCHEMISTRY

GENERAL INTRODUCTION

- Electrochemistry is the branch of physical chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions.



Materials

(on the basis of ability to carry current)

Conductors
These can pass current.

Semiconductors
Mediators

Insulators
These can not pass current.

(on the basis of species which carry current)

Electrolytic Conductors
Current flows due to motion of ions produced by electrolytes.

Metallic Conductors
Flow of current is due to motion of electrons.

(on the basis of extent of ionisation)

Weak Electrolytes
These are ionised to small extent *e.g.*, CH_3COOH, H_2CO_3, etc.

Strong Electrolytes
These are almost completely ionised *e.g.*, HCl, HNO_3, etc.

Conductance / Conductivity

Equivalent Conductivity (Λ_{eq})

$$\Lambda_{eq} = \kappa \times V\text{ (in mL)} = \kappa \times \frac{1000}{C} = \kappa \times \frac{1000}{N}$$

Unit = S cm^2 eq^{-1} or Ω^{-1} cm^2 eq^{-1}

Specific Conductance or Conductivity (κ)

$$\kappa = G \times \frac{l}{a} = \frac{1}{R} \times \frac{l}{a}$$

$\frac{l}{a}$ = cell constant

Unit = S m^{-1} = Ω^{-1} m^{-1}

Molar Conductivity (Λ_m)

$$\Lambda_m = \kappa \times V\text{ (in mL)} = \kappa \times \frac{1000}{M}$$

Unit = S cm^2 mol^{-1} or Ω^{-1} cm^2 mol^{-1}

Conductance (G) : $G = \frac{1}{R}$

Unit = Ω^{-1} or mho

VARIATION OF CONDUCTIVITY AND MOLAR CONDUCTIVITY WITH CONCENTRATION

- With increase in dilution, conductivity of the electrolytic solution decreases.
- In case of strong electrolytes, molar conductivity increases slowly with dilution and approaches a certain limiting value when concentration approaches zero (infinite dilution) and is given by *Debye Huckel Onsager equation*.

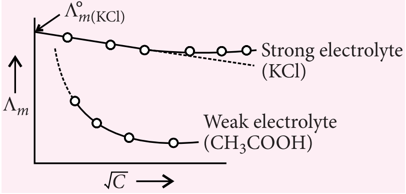
  $$\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$$

  Here, Λ_m° = Limiting molar conductivity at infinite dilution

  Λ_m = Molar conductivity

  A = Constant which depends upon nature of solvent and temperature

  C = Concentration
- In case of weak electrolytes, the molar conductivity is low as compared to that of strong electrolytes.



KOHLRAUSCH'S LAW

- At infinite dilution, $\Lambda_m^\circ = \lambda^\circ(\text{cation}) + \lambda^\circ(\text{anion})$

  for A_xB_y ; $\Lambda_m^\circ = x\lambda_+^\circ + y\lambda_-^\circ$

ELECTROLYSIS

- The passage of charge through an electrolyte brings chemical changes involving reduction as well as oxidation of ions, the phenomenon is known as electrolysis.

Electrolysis

Electrolytic Cell

The device in which the process of electrolysis is carried out, is called electrolytic cell.

- Oxidation at anode.
- Reduction at cathode.
- Cathodic reaction will be with higher E°_{red} value.
- Anodic reaction will be with higher E°_{ox} value.

Faraday's Law of Electrolysis

- First law of electrolysis :

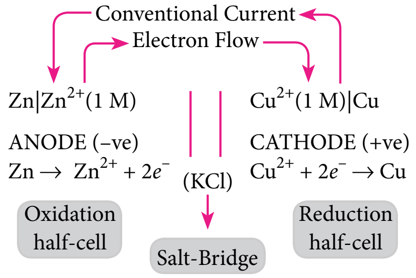
  $m \propto Q \propto (I \times t) = ZIt$

  (m = mass liberated at electrode,
  Q = quantity of electricity
  Z = electrochemical equivalent)
- Second law of electrolysis :

  $$\frac{\text{Mass of } x}{\text{Mass of } y} = \frac{\text{Chemical equivalent mass of } x}{\text{Chemical equivalent mass of } y} = \frac{Z_x}{Z_y}$$
- 1 Faraday (1F) = 96,500 coulombs

ELECTROCHEMICAL CELL

- The device in which chemical energy is converted into electrical energy is called galvanic cell or electrochemical cell or voltaic cell.



ELECTRODE POTENTIAL

- The electrode potential is the tendency of an electrode to lose or gain electrons when it is in contact with the solution of it own ions.
- **EMF or Cell Potential :** The difference in electrode potentials of the two electrodes of the cell is known as EMF or Cell potential.

$$E^\circ_{cell} = E^\circ_{ox(anode)} + E^\circ_{red(cathode)}$$

$$= E^\circ_{red(cathode)} - E^\circ_{red(anode)} \qquad [\because\ E^\circ_{ox} = -E^\circ_{red}]$$

$$= E^\circ_{red\ (right)} - E^\circ_{red\ (left)}$$

Electrode Potential

Oxidation Potential (E°_{ox})

When electrode is negative charged (anode), oxidation occurs.

$M \rightarrow M^{n+} + ne^-$

Potential of oxidation half reaction $= E^\circ_{ox}$

Reduction Potential (E°_{red})

When electrode is positively charged (cathode), reduction occurs.

$M^{n+} + ne^- \rightarrow M$

Potential of reduction half reaction $= E^\circ_{red}$

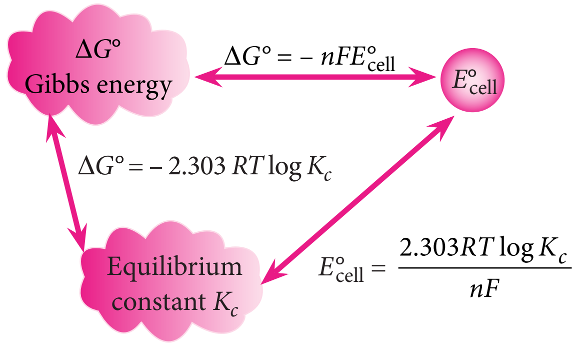
Standard Electrode Potential

The potential difference developed between metal electrodes and the solution of its ions of 1 M at 25°C.

NERNST'S EQUATION

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

RELATIONSHIP BETWEEN ELECTRODE POTENTIAL, GIBBS ENERGY AND EQUILIBRIUM CONSTANT



INFO SHOTS

Li-S batteries : Firing for compactness !

Conventional Li-S batteries have a non-compact cathode structure containing low areal loading of active materials. Now, a strategy of burning Li foils in a CS_2 vapour is presented, which leads to the formation of highly compact Li_2S nano-particles as a lithiated sulphur cathode, offering promising battery performance.

BATTERIES

- The term battery is used when two or more galvanic cells are connected in series.

Batteries

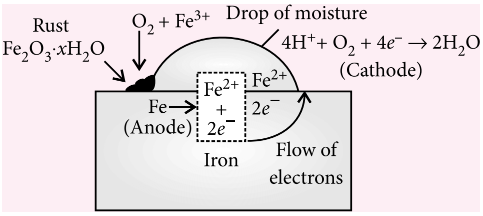
- **Primary Batteries**
  - Not rechargeable, *e.g.*, voltaic cell, mercury cell, Leclanche cell.
- **Secondary Batteries**
  - Rechargeable *e.g.*, lead-storage batteries, nickel-cadmium storage batteries.

Cell	Cathode/Anode	Electrolyte	Cell reactions
Dry cell	Graphite/Zinc	$MnO_2 + C$ (Around cathode) $NH_4Cl + ZnCl_2$ (Around anode)	**Anode :** $Zn \rightarrow Zn^{2+} + 2e^-$ **Cathode :** $MnO_{2(s)} + NH^+_{4(aq)} + e^- \rightarrow MnO(OH) + NH_3] \times 2$ $Zn + 2MnO_{2(s)} + 2NH^+_{4(aq)} \rightarrow Zn^{2+} + 2MnO(OH) + 2NH_3$
Mercury cell	Hg(II) oxide/ Zinc	Paste of KOH and ZnO	**Anode :** $Zn(Hg) + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O + 2e^-$ (Amalgam) **Cathode :** $HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-_{(aq)}$ $Zn(Hg) + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$
Lead storage cell	Lead packed with PbO_2/Lead	38% H_2SO_4 solution	**Anode :** $Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$ **Cathode :** $PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$ $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$
Nickel - Cadmium storage cell	NiO_2/Cd	KOH solution	**Anode :** $Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_2 + 2e^-$ **Cathode :** $2NiO_{2(s)} + 2H_2O_{(l)} + 2e^- \rightarrow Ni(OH)_2 + 2OH^-_{(aq)}$ $Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_2 + Ni(OH)_2$

CORROSION

- Corrosion is a process of deterioration of a metal as a result of its reaction with air or water (environment) surrounding it.
- Corrosion of iron is known as rusting. Rust is hydrated form of ferric oxide, $Fe_2O_3 . xH_2O$.

MECHANISM OF RUSTING

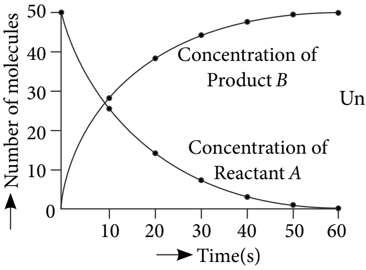


CHEMICAL KINETICS

RATE OF A CHEMICAL REACTION

- Change in the concentrations of reactants or products per unit time is known as rate of reaction.
  Progress of a reaction : Reactant, $A \longrightarrow$ Product, B
  For a reaction : $aA + bB \longrightarrow cC + dD$
- Rate of reaction is defined as :

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$



Unit of rate = mol L^{-1} s^{-1}

Factors Affecting the Rate of the Reaction

Catalyst

- A substance that increases the reaction rate without undergoing a chemical change itself. Catalyst lowers the activation energy for a chemical reaction.
- Activation energy = Threshold energy − Average kinetic energy of reacting molecules.

Concentration of Reactants

- The rate of reaction increases with increase in concentration of reactants as the number of collisions increases.

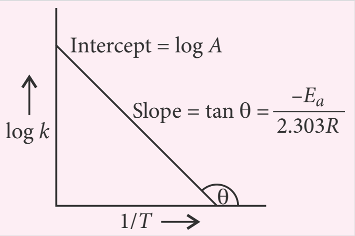
Nature of Reactants

- The reactants with weak bonds react quickly whereas reactants with strong bonds react slowly.
- Molecular reactions are slow while ionic reactions are fast.

Temperature

- As T increases, average $K.E.$ increases.
- As average $K.E.$ increases, the particles move faster so, collision energy and collision frequency increase and hence, rate increases.
- **Arrhenius equation :** $k = Ae^{-E_a/RT}$;

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$



Surface Area of Reactants

- Greater the surface area of reactants, faster is the reaction.

RATE LAW

For a reaction
$aA + bB \rightarrow cC + dD$

Law of mass action
Rate $\propto [A]^a[B]^b$

Rate law
Rate = $k[A]^m[B]^n$
m = order of reaction w.r.t. A, n = order of reaction w.r.t. B

MOLECULARITY AND ORDER OF A REACTION

Molecularity

- Number of reacting species which collide to result in reaction.
- Only positive integral values *e.g.*, 1, 2, 3 and never have negative value.
- Theoretical concept and value is derived from mechanism of reaction.

Order of the reaction

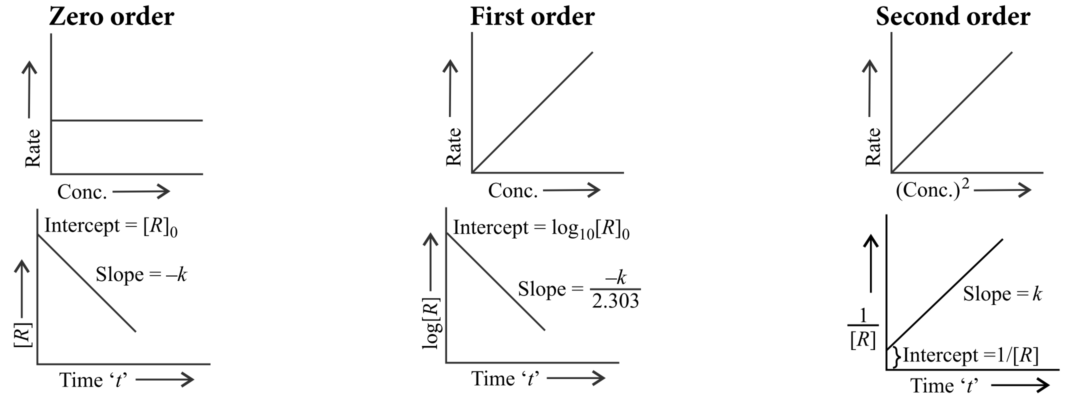
- Sum of powers to which concentration terms are raised in the rate law expression.
- Zero, fractional or even negative.
- Experimental fact and derived from rate law.

RATE LAW EXPRESSION FOR DIFFERENT ORDER REACTIONS

For the reaction : $A \longrightarrow$ Product

Reaction order *n*	Rate variation with conc.	Differential rate law	Integrated rate law	Units of rate constant	$t_{1/2}$
1	Rate doubles when $[A]$ doubles	Rate = $k[A]^1$	$\ln[A]_t / [A]_0 = -kt$	s^{-1}	$\frac{0.693}{k}$
2	Rate quadruples as $[A]$ doubles	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$L\ mol^{-1}\ s^{-1}$	$\frac{1}{k[A_0]}$
0	Rate does not change with $[A]$	Rate = $k[A]^0$	$[A]_t - [A]_0 = -kt$	$mol\ L^{-1}\ s^{-1}$	$\frac{A_0}{2k}$

Graphical Representation



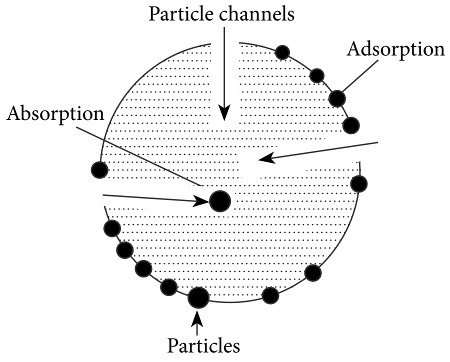
SURFACE CHEMISTRY

- Surface chemistry is a branch of chemistry that deals with phenomena, which occur at the surface.

ADSORPTION

- Existence of higher concentration of any particular component (known as adsorbate) at the surface of the liquid or solid phase (known as adsorbent).

Adsorption *vs* Absorption



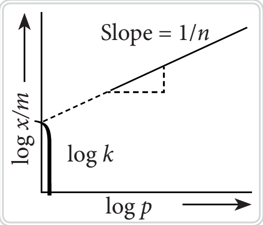
Types of Adsorption

Physical adsorption	Chemical adsorption
Caused by intermolecular van der Waals forces.	Caused by chemical bond formation.
It is not specific.	It is highly specific.
It is reversible.	It is irreversible.
Heat of adsorption is low (20-40 kJ/mol).	Heat of adsorption is high (80-240 kJ/mol).
Low temperature is favourable.	Increases with high temperature.
It forms multimolecular layers.	It forms monomolecular layers.

Adsorption Isotherms

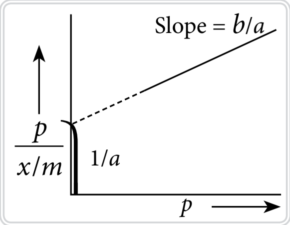
Freundlich Isotherm

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



Langmuir Isotherm

$$\frac{x}{m} = \frac{ap}{1+bp}$$



Applications of Adsorption

- To decolourise the solution
- In gas mask
- Dehumidification
- Heterogenous catalysis
- Softening of hard water
- De-ionisation of water

COLLOIDS

True solutions	Colloidal solutions	Suspensions
The solute particles having size less than 1 nm.	The particles size lies in the range of 1 nm to 1000 nm.	The size of the particles is greater than 1000 nm.
The solute particles are invisible by naked eyes as well as under the powerful microscope.	The solute particles are invisible by naked eyes but their scattering effect can be viewed with the help of a microscope.	The solute particles are visible by naked eyes and can be seen with the help of a microscope.

Types of Colloidal Solutions

Dispersed Phase	Dispersion Medium	Common Name	Examples
Solid	Solid	Solid sol	Coloured gems and glasses, some alloys, rock salt.
Solid	Liquid	Sol	Arsenious sulphide sol, gold sol, starch, paints, muddy water.
Solid	Gas	Aerosol	Smoke, dust storm.
Liquid	Solid	Gels	Jellies, cheese, iron hydroxide, shoe polish.
Liquid	Liquid	Emulsion	Milk, cod-liver oil.
Liquid	Gas	Liquid aerosol	Mist, fog, cloud, insecticide sprays.
Gas	Solid	Solid foam	Pumice stone, occluded gases, rubber.
Gas	Liquid	Foam	Soap lather, whipped cream, lemonade froth.

CONCEPT MAP

MOLECULAR ORBITAL THEORY (MOT)

MO Theory was originally called Hund-mulliken theory. The molecular orbital theory was first published in 1929 paper of Lennard-Jones. This paper notebly predicted a triplet ground state for dioxygen molecule. The orbital was introduced by Mulliken in 1932. By 1933, the molecular orbital theory has been accepted as a valid and useful theory.

Class XI

Class XII

OXIDATION REACTIONS

Oxidation reactions are very useful in organic synthesis as well as for distinguishing different organic compounds. In daily life also oxidation reactions are involved in various processes such as metabolism, photosynthesis, corrosion, rancidity, etc.

CONCEPT MAP

Chemical Bonding Models

Molecular Orbital Theory

Atomic orbitals combined to form molecular orbitals as atoms are moved towards each other.

Order of Energy of Molecular Orbitals

From H_2 to N_2 Molecules

$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2p_x) = \pi(2p_y) < \sigma(2p_z) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$

For O_2, F_2 and Ne_2 Molecules

$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < \pi(2p_x) = \pi(2p_y) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$

Merits of MOT

- Best for predicting stability of molecules.
- Best for predicting magnetic behaviour of molecules.

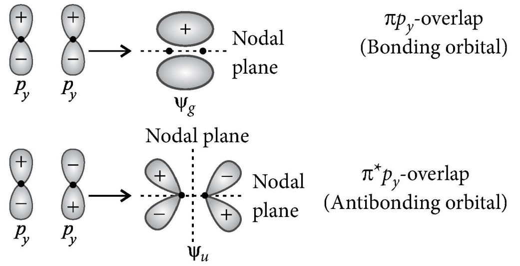
Sigma-Orbitals

Cylinderically symmetric around bond axis.

Pi-Orbitals

Perpendicular to bond axis.

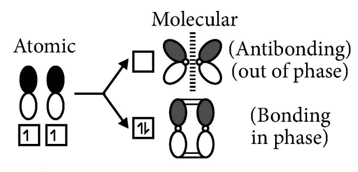
p-p sidewise overlapping :

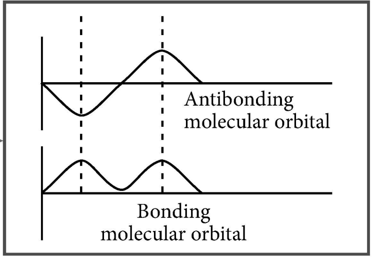


Valence Bond Theory

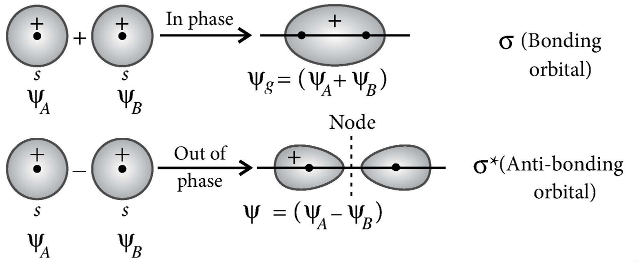
Bonding electrons occupy orbitals of hybridised (*s*, *p*, *d*) character.

Formation of Molecular Orbitals

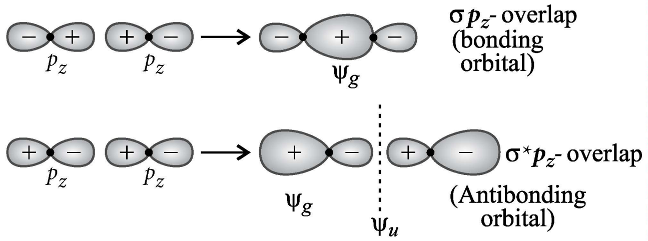




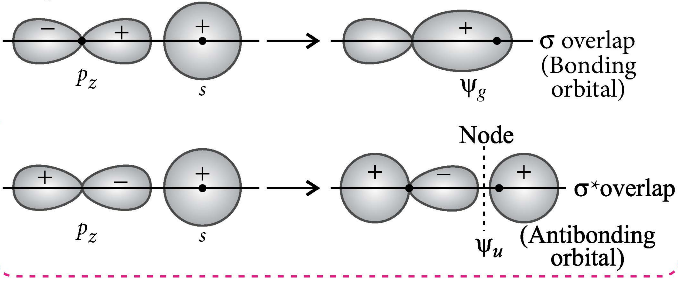
s-s overlapping :



p-p lateral overlapping :



s-p_z overlapping :

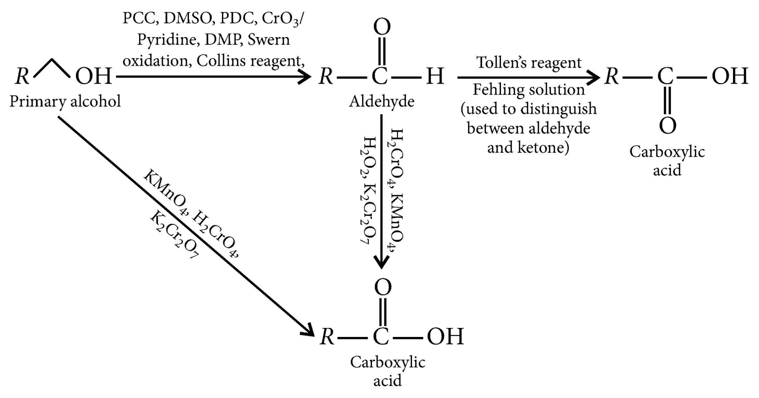


Shared Electron Pair

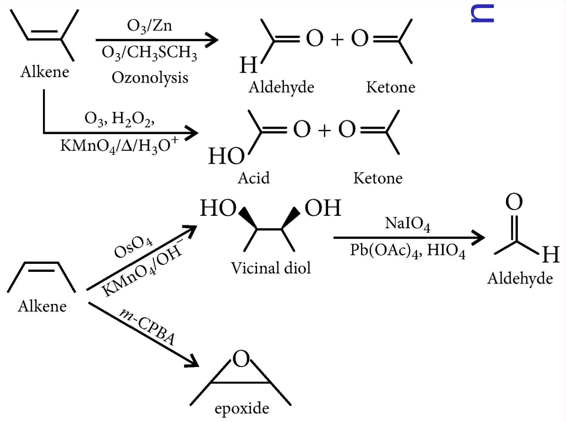
Bonding electrons occupy atomic orbitals.

Oxidation Processes

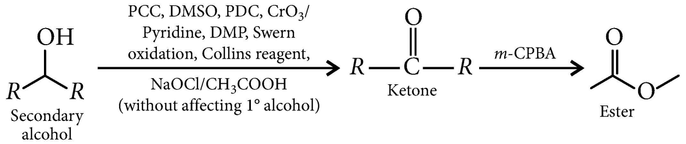
Oxidation of Primary Alcohols



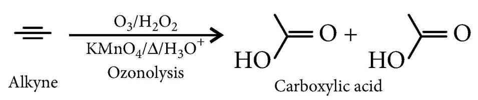
Oxidation of Alkenes



Oxidation of Secondary Alcohols

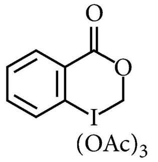


Oxidation of Alkynes



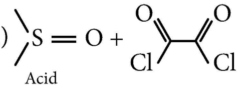
Important Reagents

1. PCC ⇒ Pyridinium chlorochromate $[C_5H_5NH]\ [CrO_3Cl]$
2. DMP ⇒ Dess – Martin Periodinane



3. Swern Oxidation ⇒ In swern oxidation, following reagents are used :

(i)



(ii) NR_3

Used to avoid the use of toxic metals such as chromium.

4. Collins reagent ⇒ It is a complex of CrO_3 with pyridine in CH_2Cl_2.
5. *m*-CPBA ⇒ *m*-Chloroperoxybenzoic acid.
6. Jones reagent ⇒ Chromic acid in aqueous acetone.

Importance of DMP Reagent

- Using periodinane has several advantages over chromium and DMSO based oxidation.
  - Milder conditions
  - Shorter reaction times
  - Higher yield
  - Simplified workups
  - High chemoselectivity
  - Tolerance of sensitive functional groups
  - Long shelf life
- Using DMP conditions, alcohols can be oxidised to aldehydes / ketones without affecting furan rings, sulphides, vinyl ethers and secondary amides.

Classification of Colloids

Classification of Colloids

Based on the nature of interactions between dispersed phase and dispersion medium

Lyophilic Sols
In such sols, the dispersed phase has greater affinity for dispersion medium *e.g.*, sols of gum, starch, protein etc.

Lyophobic Sols
In such sols, dispersed phase has little affinity for the dispersion medium *e.g.*, sols of metals, metal oxides, etc.

Based on the type of particles of dispersed phase

Multimolecular Colloids
In this type of colloids, the colloidal particles are aggregates of atoms or small molecules with molecular size less than 1 nm *e.g.*, gold sol, sulphur sol, etc.

Macromolecular Colloids
In this type of colloids, colloidal particles are themselves large molecules having colloidal dimensions *e.g.*, starch, cellulose, etc.

Associated Colloids
There are certain substances which behave as normal, strong electrolytes at low concentration but at higher concentration they exhibit colloidal behaviour due to the formation of aggregated particles. The aggregated particles thus formed are called micelles. *e.g.*, soap ($C_{17}H_{35}$ COONa).

Preparation and Purification of Colloids

Preparation of Colloids	Purification of Colloids
By Bredig's arc method (for metals) : A direct current is passed through electrodes of metals suspended in a trough of ice cold water. Intense heat of the arc changes the metal into vapours which condense to form the colloidal particles.	**Dialysis :** It is the process of separating a crystalloid from a colloid by diffusion or filtration through a semipermeable membrane or dialyzing membrane. The process can be quickened by applying electric field and is called *electro-dialysis*.
Ultrasonic dispersion : Ultrasonic vibrations which have frequency more than that of sound are made to strike a beaker containing the substances (oils, sulphur, sulphides and oxides of metals) to be dispersed by using water as the dispersion medium.	**Ultrafiltration :** It is the process of separating the colloidal particles by filtration through ultrafilter paper which is obtained by treating ordinary filter paper with gelatine solution.
Peptization : A freshly prepared precipitate is converted into colloidal particles by adding a suitable electrolyte, called peptizing agent.	**Ultra-centrifugation :** In this method, the impure sol is taken in a tube which is placed in an ultracentrifuge and rotated at a very high speed.

Coagulation of Colloids

- The precipitation of colloids through induced aggregation by addition of some suitable electrolytes is called coagulation or flocculation.

INFOSHOTS

Surface chemistry : Giving catalysts a hand !

Using chiral modifiers on the surfaces of heterogeneous catalysts is a potentially fruitful route to practical stereoselective chemistry. Now, a study of the dynamics of prochiral adsorbates on modified surfaces has shown that they can rapidly interconvert between adsorption states of different prochirality.

- **Hardy Schulze Rule :** Coagulating power of an electrolyte depends on the valency of oppositely charged ion. Greater the valency of oppositely charged ion, more is the coagulating power.
- **Gold Number :** The number of milligrams of the protective colloid which just prevent coagulation of 10 mL of standard gold sol when 1 mL of 10% solution of sodium chloride is added to it.

Properties of Colloids

Properties of Colloids

Filterability
These cannot pass through parchment paper.

Non-settling
They tend to settle down very slowly.

Colligative properties
They possess very low values of colligative properties .

Tyndall effect
The scattering of light by the colloidal particles present in a colloidal sol is known as Tyndall effect.

Electrophoresis
The movement of colloidal particles towards oppositely charged electrodes under the influence of electric field is known as electrophoresis.

Electro-osmosis
The movement of the molecules of the dispersion medium under the influence of electric field whereas colloidal particles are not allowed to move.

Brownian Movement
Colloidal particles exhibit continuous zig-zag motion which is known as Brownian movement.

EMULSIONS

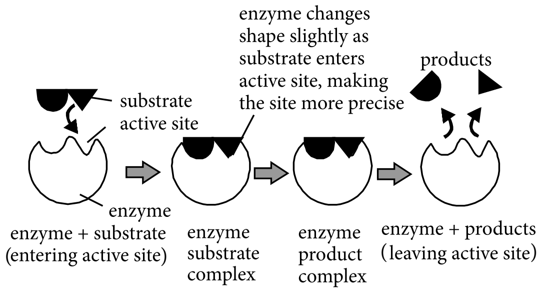
- Emulsions are the colloidal systems in which both the dispersed phase and dispersion medium are liquids.

Types of Emulsions

- **Oil in water (*O/W*) type :** In this type of emulsion, oil is the dispersed phase and water is the dispersion medium. Milk is an emulsion of *O/W* type, where fat globules are dispersed in water.
- **Water in oil (*W/O*) type :** In this type of emulsion, water is the dispersed phase and oil is the dispersion medium. Butter is an emulsion of *W/O* type.

CATALYST

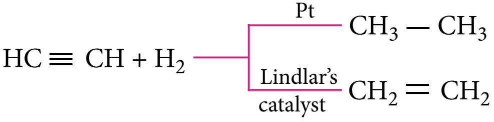
- Catalysts speed up a chemical reaction without being used up.



Important Properties of Catalysts

Activity : A catalyst may accelerate a reaction to as high as 10^{10} times.

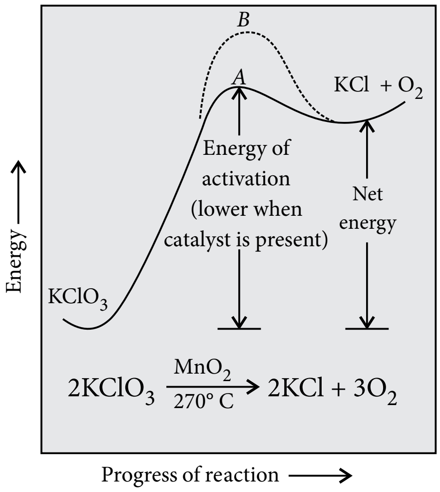
Selectivity : Ability to direct a reaction to give particular product *e.g.*,



$$HC \equiv CH + H_2 \xrightarrow{Pt} CH_3 - CH_3$$

$$HC \equiv CH + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar's}} CH_2 = CH_2$$

Effect of Catalyst



A : Curve in presence of catalyst
B : Curve in absence of catalyst

Types of catalysis

- **Based on effect of catalyst :**
  - **Positive catalysis**
    Increases the rate of reaction.
    $2KClO_3 \xrightarrow[270^\circ C]{MnO_2} 2KCl + 3O_2$
  - **Negative catalysis**
    Decreases or retard the rate of reaction.
    $2CHCl_3 + O_2 \xrightarrow{\text{Alcohol}} 2COCl_2 + 2HCl$
  - **Auto-catalysis**
    When one of the product act as a catalyst.
    $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$
- **Based on phase catalyst :**
  - **Homogeneous catalysis**
    Catalyst is in the same phase as the reactants.
    Hydrolysis of ester (dil. acid as catalyst).
    Oxidation of SO_2 to SO_3 in lead chamber process (Catalyst is NO).
  - **Heterogeneous catalysis**
    The catalyst is in the different phase from the reactants.
    1. Ammonia synthesis (Catalyst : Fe with Al_2O_3)
    2. Methanol synthesis
       (Catalyst : ZnO/Cr_2O_3)

SPEED PRACTICE

1. The electrolysis of a metal salt solution was carried out by passing a current of 4 amperes for 45 minutes. It results in deposition of 2.977 g of a metal. If atomic mass of the metal is 106.4 g mol^{-1}. Calculate the charge on the metal cation.
(a) +4 (b) +3 (c) +2 (d) +1

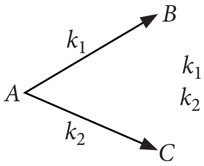
2. The decomposition of N_2O_5 is a first order reaction represented by $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$. After 15 minutes the volume of O_2 produced is 9 mL and at the end of the reaction 35 mL. The rate constant is equal to
(a) $\frac{1}{15}\ln\frac{35}{44}$ (b) $\frac{1}{15}\ln\frac{44}{26}$
(c) $\frac{1}{15}\ln\frac{44}{35}$ (d) $\frac{1}{15}\ln\frac{35}{26}$

3. Air can oxidise sodium sulphite in aqueous solution but cannot do so in the case of sodium arsenite. If however, air is passed through a solution containing both sodium sulphite and sodium arsenite then both are oxidised. This is an example of
(a) positive catalysis (b) negative catalysis
(c) induced catalysis (d) autocatalysis.

4. Two students use same stock solution of $ZnSO_4$ and different stock solutions of $CuSO_4$. The emf of one of the cell is 0.03 V higher than the other. The conc. of $CuSO_4$ in the cell with higher emf is 0.5 M. Calculate the conc. of $CuSO_4$ in the other cell. ($2.303\ RT/F = 0.06$)
(a) 1 M (b) 0.05 M (c) 1.5 M (d) 0.25 M

5. A solution of a mixture of organic compounds in a suitable solvent is poured in a vertical column of an adsorbent followed by dripping of solvent. As the solvent percolates down the column
(a) all the components remain adsorbed at the top of the column
(b) the various components run down the column to the same distance
(c) the most strongly adsorbed component runs down farthest
(d) the most weakly adsorbed component runs down farthest.

6. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as



$k_1 = 1.26 \times 10^{-4} s^{-1}$
$k_2 = 3.8 \times 10^{-5} s^{-1}$

The percentage distribution of B and C are
(a) 74.12% B and 25.88% C
(b) 80.29% B and 19.71% C
(c) 76.83% B and 23.17% C
(d) 89.55% B and 10.45% C.

7. For the following electrochemical cell at 298 K,
$Pt_{(s)}|H_{2(g)}, (1\ bar)|H^+_{(aq)}, (1\ M)||M^{4+}_{(aq)}|M^{2+}_{(aq)}|Pt_{(s)}$
$E_{cell} = 0.092$ V when $\frac{[M^{2+}_{(aq)}]}{[M^{4+}_{(aq)}]} = 10^x$

(Given : $E^\circ_{M^{4+}/M^{2+}} = 0.151\text{ V};\ 2.303\dfrac{RT}{F} = 0.059\text{ V}$)

The value of x is

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

(JEE Advanced 2016)

8. Find the two-third life, $t_{2/3}$, of a first order reaction in which $k = 5.4 \times 10^{-14}\text{ s}^{-1}$.

(a) 5.4×10^{14} s (b) 1.85×10^{13} s

(c) 2.03×10^{13} s (d) 1.58×10^{14} s

9. A freshly obtained precipitate of SnO_2 is peptised by little of KOH to give a sol. The sol particles may be represented as

(a) $[SnO_2]K^+$ (b) $[SnO_2]OH^-$

(c) $[SnO_2]Sn^{4+}$ (d) $[SnO_2]SnO_3^{2-} : 2K^+$

10. Standard electrode potential for Sn^{4+}/Sn^{2+} couple is +0.15 V and that for the Cr^{3+}/Cr couple is −0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be

(a) + 1.83 V (b) + 1.19 V

(c) + 0.89 V (d) + 0.18 V

11. In a biomolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are)

(a) experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation

(b) the value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

(c) the activation energy of the reaction is unaffected by the value of the steric factor

(d) since $P = 4.5$, the reaction will not proceed unless an effective catalyst is used.

(JEE Advanced 2017)

12. In an adsorption experiment, a graph between $\log(x/m)$ versus $\log p$ was found to be linear with a slope of 45°. The intercept on the $\log(x/m)$ axis was found to be 0.3010. Calculate the amount of the gas adsorbed per gram of charcoal under the pressure of 0.6 bar.

(a) 0.6 (b) 1.2 (c) 0.18 (d) 1.8

13. Two reactions, $P \rightarrow$ products and $Q \rightarrow$ products have rate constants k_P and k_Q at temperature, T and activation energies E_P and E_Q respectively. If $k_P > k_Q$ and $E_P < E_Q$ and assuming that A for both the reactions is same then

(a) at higher temperature k_P will be greater than k_Q

(b) at lower temperature k_P and k_Q will differ more and $k_P > k_Q$

(c) as temperature rises k_P and k_Q will be close to each other in magnitude

(d) all of these.

14. The correct order of $E^\circ_{M^{2+}/M}$ values with negative sign for the four successive elements Mn, Fe, Co and Ni is

(a) Ni > Mn > Fe > Co (b) Mn > Fe > Co > Ni

(c) Ni > Fe > Mn > Co (d) Fe > Mn > Ni > Co

15. The following statements relate to the adsorption of gases on a solid surface. Identify the incorrect statement among them.

(a) Enthalpy of adsorption is negative.

(b) Entropy of adsorption is negative.

(c) On adsorption, the residual forces on the surface are increased.

(d) On adsorption decrease in surface energy appears as heat.

(JEE Main Online 2015)

16. The rate equation for the reaction : $2A + B \rightarrow C$ is found to be, rate $= k[A][B]$. The correct statement in relation to this reaction is that the

(a) units of k must be s^{-1}

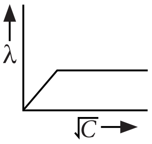
(b) $t_{1/2}$ is constant

(c) rate of formation of C is same as the rate of disappearance of A

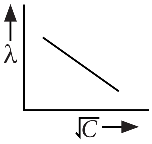
(d) value of k is independent of the initial concentration of A and B.

17. The variation of equivalent conductance of weak electrolyte with $\sqrt{C}$ is correctly shown in which of the following figures?

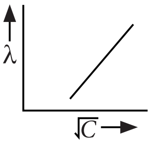
(a)



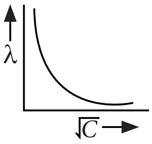
(b)



(c)



(d)



18. Which of the following statements is not true about the oil-in-water type emulsion?

(a) On addition of small amount of water, no separate layer of water appears.

(b) On addition of oil, separate layer of oil is formed.

(c) Addition of an electrolyte causes the conductivity of the emulsion to increase.

(d) Addition of small amount of oil soluble dye renders the entire emulsion coloured.

19. If the E°_{cell} for a given reaction has a negative value, which of the following gives the correct relationships for the values of ΔG° and K_{eq}?

(a) $\Delta G^\circ > 0; K_{eq} < 1$ (b) $\Delta G^\circ > 0; K_{eq} > 1$
(c) $\Delta G^\circ < 0; K_{eq} > 1$ (d) $\Delta G^\circ < 0; K_{eq} < 1$

(NEET Phase-II 2016)

20. The concentration of R in the reaction, $R \rightarrow P$, was measured as a function of time and the following data is obtained :

[R] (molar)	1.0	0.75	0.40	0.10
t (min.)	0.0	0.05	0.12	0.18

The order of the reaction is

(a) 0 (b) 1 (c) 2 (d) 3

21. The volumes of gases H_2, CH_4, CO_2 and NH_3 adsorbed by 1 g of activated charcoal at 298 K are in the order

(a) $H_2 > CH_4 > CO_2 > NH_3$
(b) $CH_4 > CO_2 > NH_3 > H_2$
(c) $CO_2 > NH_3 > H_2 > CH_4$
(d) $NH_3 > CO_2 > CH_4 > H_2$

22. The rate of first-order reaction is 0.04 mol L^{-1} s^{-1} at 10 seconds and 0.03 mol L^{-1} s^{-1} at 20 seconds 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 Phase-I 2016)

23. Which has minimum potential for the half cell reaction : $2H^+ + 2e^- \longrightarrow H_2$?

(a) 1·0 M HCl (b) 1·0 M NaOH
(c) Pure water (d) A solution with pH = 4

24. The charge of colloidal particles can be determined by the phenomenon

(a) electrodialysis (b) electrophoresis
(c) Bredig's arc method (d) electro-osmosis.

25. For the reaction : $4KClO_3 \rightarrow 3KClO_4 + KCl$

if $\dfrac{-d[KClO_3]}{dt} = k_1[KClO_3]^4$

$\dfrac{d[KClO_4]}{dt} = k_2[KClO_3]^4$

$\dfrac{d[KCl]}{dt} = k_3[KClO_3]^4$, the correct relation between k_1, k_2 and k_3 is

(a) $k_1 = k_2 = k_3$ (b) $4k_1 = 3k_2 = k_1$
(c) $3k_1 = 4k_2 = 12k_3$ (d) none of these.

26. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its dissociation constant. (Given $\lambda^\circ_{(H^+)}$ = 349.6 S cm^2 mol^{-1} and $\lambda^\circ_{(HCOO^-)}$ = 54.6 S cm^2 mol^{-1}.)

(a) 3.14×10^{-3} (b) 3.67×10^{-4}
(c) 4.15×10^{-4} (d) 5.21×10^{-3}

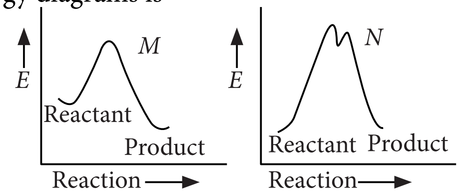
27. A gelatin gel containing $K_2Cr_2O_7$,was filled in a test tube and a concentrated solution of $AgNO_3$ was added on the top. Dark red Ag_2CrO_4 precipitate is formed

(a) uniformly downward with decreasing concentration
(b) in the form of rings equally spaced and equally intense
(c) in the form of rings of decreasing intensity and increasing spacings
(d) in the form of rings of decreasing intensity but of equal spacings.

28. Select the correct statement.

(a) (E) Efficiency of a fuel cell is given by the equation $E = \dfrac{\Delta G}{\Delta H} \times 100$.
(b) The efficiency (E) for H_2/O_2 fuel cell is 83%.
(c) The efficiency (E) for H_2/O_2 fuel cell depends upon temperature at which it works.
(d) All the above statements are correct.

29. The correct statement regarding the following energy diagrams is



(a) Reaction M is faster and less exothermic than reaction N
(b) Reaction M is slower and less exothermic than reaction N
(c) Reaction M is faster and more exothermic than reaction N
(d) Reaction M is slower and more exothermic than reaction N.

30. Which one of the following statements is not correct?

(a) The value of equilibrium constant is changed in the presence of a catalyst in the reaction at equilibrium.
(b) Enzymes catalyse mainly bio-chemical reactions.
(c) Coenzymes increase the catalytic activity of enzyme.
(d) Catalyst does not initiate any reaction.

(NEET 2017)

SOLUTIONS

1. **(a)** : Let the charge on the metal ion be n^+.

$\therefore$ The reduction half-reaction would be

$$\underset{(1\ \text{mol})}{M^{n+}} + \underset{(n\ \text{mol})}{ne^-} \longrightarrow \underset{(1\ \text{mol} = 106.4\ \text{g})}{M}$$

Quantity of electricity required for depositing 106.4 g of metal = $n \times 96500$ C

Quantity of electricity required for depositing 2.977 g of metal

$$= \frac{n \times 96500 \times 2.977}{106.4} = n \times 2700\ \text{C}$$

Quantity of electricity actually passed

$= 4 \times 45 \times 60 = 10800$ C

Now, $10800 = n \times 2700$

$$\therefore \quad n = \frac{10800}{2700} = 4$$

Hence, charge on metal ion = + 4

2. **(d)** : $k = \frac{1}{t}\ln\left(\frac{a}{a-x}\right) = \frac{1}{15}\ln\left(\frac{35}{35-9}\right) = \frac{1}{15}\ln\frac{35}{26}$

3. **(c)**

4. **(b)** : Let the two cells be

$Zn|Zn^{2+}\ (C_1)\ ||\ Cu^{2+}\ (C)|Cu$; emf = E_1

$Zn|Zn^{2+}\ (C_2)\ ||\ Cu^{2+}\ (0.5\ M)|Cu$; emf = E_2

According to question, $C_1 = C_2$;

$E_2 - E_1 = 0.03$ ...(i)

According to Nernst equation,

$$E_1 = E^\circ_{cell} + \frac{0.06}{2}\log\frac{C}{C_1} \quad \text{...(ii)}$$

$$E_2 = E^\circ_{cell} + \frac{0.06}{2}\log\frac{0.5}{C_2} \quad \text{...(iii)}$$

From equations (i), (ii) and (iii),

$$\therefore \quad \frac{0.06}{2}\left[\log\frac{C_1}{C}\times\frac{0.5}{C_2}\right] = 0.03$$

$$\therefore \quad \log\frac{0.5}{C} = \frac{2\times 0.03}{0.06} = 1 \Rightarrow C = 0.05\ M$$

5. **(d)**

6. **(c)** : % distribution of $B = \frac{k_1}{k_1+k_2}\times 100$

$$= \frac{1.26\times 10^{-4}}{1.26\times 10^{-4} + 3.8\times 10^{-5}}\times 100$$

$B\% = 76.83\%$

% distribution of $C = \frac{k_2}{k_1+k_2}\times 100$

$$= \frac{3.8\times 10^{-5}}{1.26\times 10^{-4} + 3.8\times 10^{-5}}\times 100$$

$C\% = 23.17\%$

7. **(d)**: For the given electrochemical cell, the reactions are

At anode : $H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$

At cathode : $M^{4+}_{(aq)} + 2e^- \rightarrow M^{2+}_{(aq)}$

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

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

$$0.092 = \left(E^\circ_{M^{4+}/M^{2+}} - E^\circ_{H^+/H_2}\right) - \frac{0.059}{2}\log(10^x[H^+]^2)$$

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

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

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

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

$10^x = \text{Antilog } 2 = 10^2 \Rightarrow x = 2$

8. **(c)** : The rate constant k for first order reaction is

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \quad \text{or} \quad t = \frac{2.303}{k}\log\frac{a}{a-x}$$

Substitute,

$$t = t_{2/3},\ k = 5.4\times 10^{-14}\ s^{-1},\ x = \frac{2a}{3}$$

$$t_{2/3} = \frac{2.303}{5.4\times 10^{-14}}\log\frac{a}{a-\frac{2}{3}a} = \frac{2.303}{5.4}\times 10^{14}(\log 3)$$

$= 0.4265 \times 0.477 \times 10^{14}$ s $= 2.03 \times 10^{13}$ s

9. **(d)** : $SnO_{2(s)} + 2KOH_{(aq)} \rightarrow K_2SnO_{3(aq)} + H_2O$

$K_2SnO_3 \rightleftharpoons 2K^+ + SnO_3^{2-}$

Here, SnO_3^{2-} are retained on the double layer while K^+ ions go in the dispersion medium.

$[SnO_2]SnO_3^{2-} : 2K^+$

10. **(c)** : $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= 0.15 - (-0.74) = +0.89$ V

11. **(a, c)** : Arrhenius equation is

$k = Ae^{-Ea/RT}$

where, A = Frequency factor

Taking into account orientation factor,

$k = PZ_{AB}\, e^{-Ea/RT}$

where, P = steric factor, Z_{AB} = collision frequency

The value of steric factor lies between 0 and 1 predicted by Arrhenius equation. Thus, the experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation.

The activation energy of the reaction does not depend upon the value of the steric factor.

If P is very small, then catalyst is required to carry out the reaction at measurable rate.

12. (b) : According to Freundlich equation,

$$\frac{x}{m} = kp^{1/n} \text{ or } \log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

$\therefore$ Plot of $\log\frac{x}{m}$ versus $\log p$ is linear with slop $= \frac{1}{n}$

x = Intercept = $\log k$.

Thus, $\frac{1}{n} = \tan\theta \Rightarrow \tan 45° = 1 \quad \therefore\ n = 1$

$\log k = 0.3010$ or k = Antilog 0.3010 = 2

At $p = 0.6$ bar, $\frac{x}{m} = kp^{1/n} = 2 \times (0.6)^1 = 1.2$

13. (d)

14. (b) : Order of standard reduction potential:
Mn > Fe > Co > Ni
(According to electrochemical series)

15. (c) : After adsorption, there is decrease in the residual forces due to bond formation. ΔG, ΔH and ΔS, all are negative in the case of adsorption.

16. (d)

17. (d) : λ *vs* $\sqrt{C}$ curves are hyperbolic for weak electrolytes because on dilution number of ions as well as ionic mobility both increase for weak electrolytes.

18. (d) : Since oil is the inner (dispersed) phase, the added dye will not be dissolved in the emulsion.

19. (a) : $\Delta G° = -nFE°_{cell}$
If $E°_{cell}$ is – ve then $\Delta G°$ will be +ve *i.e.*; $\Delta G° > 0$
$\Delta G° = -nRT \log K_{eq}$
For $\Delta G°$ = +ve, K_{eq} = –ve *i.e.*, $K_{eq} < 1$

20. (a) : For zero order reaction, the rate law is written as :

$$k_1 = \frac{x}{t} = \frac{0.25}{0.05} = 5,\ k_2 = \frac{x}{t} = \frac{0.60}{0.12} = 5,\ k_3 = \frac{x}{t} = \frac{0.90}{0.18} = 5$$

As the value of rate constant remains constant by applying zero order rate law, thus, the order of the given reaction is zero.

21. (d)

22. (c) : For a first order reaction, $A \longrightarrow$ Products and for concentration of the reactant at two different times,

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

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

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

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

23. (b) : For $2\,H^+ + 2e^- \longrightarrow H_2$,

$$E = E° - \frac{0.0591}{2}\log\frac{1}{[H^+]^2}$$

$= 0.0591 \log [H^+] = -0.0591$ pH

(a) $[H^+] = 1$ M, $E = 0.0591 \log 1 = 0$

(b) $[OH^-] = 10^0$, $[H^+] = 10^{-14}$ M, pH = 14
$E = -0.0591 \times 14 = -0.827$ V

(c) $[H^+] = 10^{-7}$, pH = 7, $E = -\ 0.0591 \times 7 = -0.414$ V

(d) pH = 4, $E = -0.0591 \times 4 = -0.236$ V

24. (b)

25. (c) : Rate $= -\frac{1}{4}\frac{d[KClO_3]}{dt} = \frac{1}{3}\frac{d[KClO_4]}{dt} = \frac{d[KCl]}{dt}$

$$\therefore\ \frac{k_1}{4}[KClO_3]^4 = \frac{k_2}{3}[KClO_3]^4 = k_3[KClO_3]^4$$

$\therefore\ 3k_1 = 4k_2 = 12k_3$

26. (b) : $\Lambda°_{(HCOOH)} = \lambda°_{(H^+)} + \lambda°_{(HCOO^-)}$

$= 349.6 + 54.6 = 404.2$ S cm^2 mol^{-1}

$$\frac{\Lambda_m^c}{\Lambda_m^{\circ}} = \frac{46.1}{404.2} = 0.114$$

	$HCOOH \rightleftharpoons$	$HCOO^-$	$+\ H^+$
Initial conc.	C mol L^{-1}	0	0
Conc. at eq.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{1-0.114} = 3.67 \times 10^{-4}$$

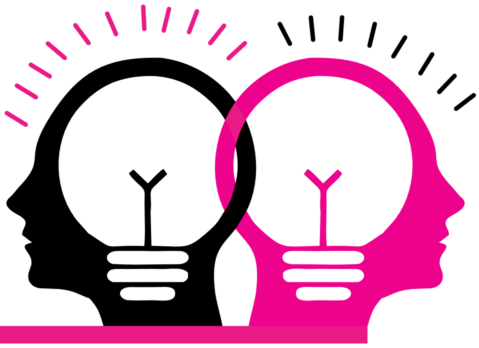
27. (c) : In the gel, the precipitation takes place in the form of bands or rings (Liesegang ring phenomenon) which have decreasing concentrations (or intensity) and increasing spacings.

28. (d) **29. (c)**

30. (a) : Calatyst does not change the value of equilibrium constant as they affect forward as well as backward reactions equally.

◆◆

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

1. A liquid is in equilibrium with its vapours at its boiling point. On average, the molecules in the two phases have equal
(a) intermolecular forces
(b) potential energy
(c) total energy (d) kinetic energy.

2. The mass of a non-volatile solute (molecular mass = 40) which should be dissolved in 114 g octane to reduce its vapour pressure to 80% is
(a) 10 g (b) 5 g (c) 7.5 g (d) 12 g

3. The substance whose solubility increases with increase in temperature is
(a) $NaNO_3$ (b) KCl
(c) KNO_3 (d) all of these.

4. At a given temperature, osmotic pressure of a concentrated solution of its substance
(a) is higher than that of its dilute solution
(b) is lower than that of its dilute solution
(c) is same as that of its dilute solution
(d) cannot be compared with osmotic pressure of its dilute solution.

5. Which of the following has been arranged in the increasing order of freezing point?
(a) 0.025 M KNO_3 < 0.1 M NH_2CSNH_2 < 0.05 M $BaCl_2$ < 0.1 M NaCl
(b) 0.1 M NaCl < 0.05 M $BaCl_2$ < 0.1 M NH_2CSNH_2 < 0.025 M KNO_3
(c) 0.1 M NH_2CSNH_2 < 0.1 M NaCl <0.05 M $BaCl_2$ < 0.025 M KNO_3
(d) 0.025 M KNO_3 < 0.05 M $BaCl_2$ < 0.1 M NaCl < 0.1 M NH_2CSNH_2

6. A solution containing 66 g of acetone and 46 g of water has a density of 0.926 g/cc. What will be the molarity of water in this solution?
(a) 26.51 M (b) 12.09 M
(c) 21.08 M (d) 14.58 M

7. Molal depression constant for water is 1.86 °C kg mol^{-1}. The freezing point of a 0.05 molal solution of a non-electrolyte in water is
(a) –1.86 °C (b) –0.93 °C
(c) –0.093 °C (d) 0.93 °C

8. Vapour pressure of pure '*A*' is 70 mm of Hg at 25 °C. It forms an ideal solution with '*B*' in which mole fraction of *A* is 0.8. If the vapour pressure of the solution is 84 mm of Hg at 25 °C, the vapour pressure of pure '*B*' at 25 °C is

(a) 56 mm of Hg (b) 70 mm of Hg
(c) 140 mm of Hg (d) 28 mm of Hg

9. At 300 K, 36 g of glucose present per litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?

(a) 0.051 M (b) 0.061 M
(c) 0.041 M (d) 0.031 M

10. Henry's law constant for the solution of methane in benzene at 298 K is 4.27×10^5 mm Hg. Calculate the mole fraction of methane in benzene at 298 K under the pressure of 760 mm Hg.

(a) 1.78×10^{-3} (b) 1.78×10^{-2}
(c) 5.61×10^2 (d) 5.61×10^3

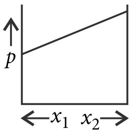
SECTION - II

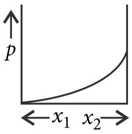
More than One Options Correct Type

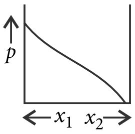
11. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statements are

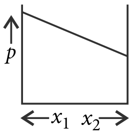
(a) ΔG is positive (b) ΔS_{system} is positive
(c) $\Delta S_{surroundings} = 0$ (d) $\Delta H = 0$

12. For a binary ideal liquid solution, the variation in total vapour pressure versus composition of solution is given by which of the following curves?

(a) 

(b) 

(c) 

(d) 

13. The solutions which are isotonic with 6% (*w*/*V*) solution of urea are

(a) 18% (*w*/*V*) solution of glucose
(b) 0.5 M solution of $BaCl_2$
(c) 1 M solution of sucrose
(d) 1 M solution of acetic acid.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

A solution containing 0.1 mole of naphthalene and 0.9 mole of benzene is cooled out until some benzene freezes out. The solution is then decanted from the solid and warmed to 353 K where its vapour pressure was found to be 670 torr. The freezing and normal boiling points of benzene are 278.5 K and 353 K respectively, $\Delta H_f = 10.67$ kJ mol^{-1}.

14. Amount of solidified benzene is

(a) 1.31 g (b) 13.1 g (c) 0.134 g (d) 12.14 g

15. The temperature to which the solution was cooled originally is

(a) 261.8 K (b) 265.2 K
(c) 270.4 K (d) 276.5 K

Paragraph for Questions 16 and 17

To account for all abnormal cases (*i.e.*, those of association or dissociation of solute molecules when dissolved in a solvent), van't Hoff introduced a factor, known as van't Hoff factor, *i*.

$$i = \frac{\text{Number of particles after association or dissociation}}{\text{Number of normal solute particles}}$$

The ratio of van't Hoff factor (*i*) to the number of ions furnished by one molecule of solute is known as osmotic coefficient '*g*' *i.e.*, $g = \frac{i}{n} = \frac{\text{van't Hoff factor}}{n}$

A 0.5% aqueous solution of potassium chloride was found to freeze at 272.76 K [Given K_f of water = 1.86 K kg mol^{-1}).

16. The van't Hoff factor for this solution is approximately

(a) 1 (b) 2
(c) $\frac{1}{2}$ (d) can't be predicted.

17. What is the degree of dissociation in the case?

(a) 100% (b) 95% (c) 92% (d) 90%

SECTION - IV

Matching List Type

18. Match the bahaviour of solutions given in List I with the examples given in List II and select the correct answer using the codes given below the lists :

List I	List II
(A) Show ideal behaviour	(p) Water + Nitric acid
(B) Show –ve deviation from ideal behaviour	(q) Benzene + Acetone
(C) Show +ve deviation from ideal behaviour	(r) *n*-Hexane + *n*-Heptane
(D) Non-ideal solution	(s) Carbon tetrachloride + Chloroform

(a) A-r,s; B-p; C- q,r; D-q
(b) A-p; B-q, s; C-r; D-q
(c) A-p; B-q,r; C-r, s; D-p,q
(d) A-r; B-p; C-q,s; D-p,q,s

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

List I	List II
(A) 10.6 g Na_2CO_3 dissolved in 100 mL solution (density = 1.06 g mL^{-1})	(p) 0.1 M
(B) 34.2 g L^{-1} sucrose solution (density = 1.0342 g mL^{-1})	(q) 1 M
(C) 9.8% H_2SO_4 solution (density 1.25 g mL^{-1})	(r) 1.25 M
(D) 20% aqueous ethanol solution by volume (density = 0.938 g mL^{-1})	(s) 3.0 M

(a) A-p; B-q; C-r; D-s (b) A-q; B-p; C-s; D-r
(c) A-q; B-r; C-p; D-s (d) A-q; B-p; C-r; D-s

SECTION - V

Assertion Reason Type

20. **Assertion :** Henry's law and Raoult's law are not independent *i.e.*, one can be derived from the other.
Reason : The partial pressure is directly proportional to the mole fraction of the concerned species for ideal solution.

21. **Assertion :** The vapour pressure of 0.1 M sugar solution is more than 0.1 M KCl solution.
Reason : Lowering of vapour pressure is directly proportional to the number of species present in the solution.

22. **Assertion :** If red blood cells are removed from the body and placed in pure water, pressure inside the cells decreases.
Reason: The concentration of the salt content in the cell increases.

SECTION - VI

Integer Value Correct Type

23. If the density of a lake water is 1.25 g mL^{-1} and contain 92 g of Na^+ ions per kg of water, the molality of Na^+ ions in the lake is

24. 45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 650 g of water. The freezing point depression (in K) will be

25. Osmotic pressure of a solution obtained by mixing 100 mL of 1.4% solution of urea (mol. mass = 60) and 100 mL of 3.42% of cane sugar solution (mol. mass = 342) at 20°C is (R = 0.0821 L atm K^{-1} mol^{-1})

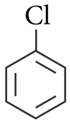
HALOALKANES AND HALOARENES

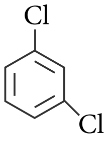
SECTION - I

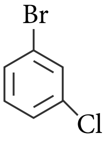
Only One Option Correct Type

1. Arrange the following compounds in the increasing order of their densities.

(i) 

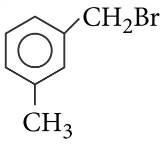
(ii) 

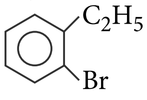
(iii) 

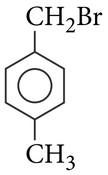
(iv) 

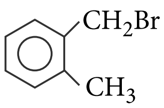
(a) (i) < (ii) < (iii) < (iv) (b) (i) < (iii) < (iv) < (ii)
(c) (iv) < (iii) < (ii) < (i) (d) (ii) < (iv) < (iii) < (i)

2. Compound (A), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A).

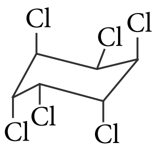
(a) 

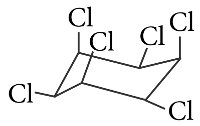
(b) 

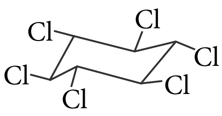
(c) 

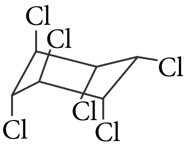
(d) 

3. Dehydrohalogenation by strong base is slowest in

(a) 

(b) 

(c) 

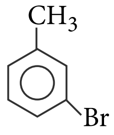
(d) 

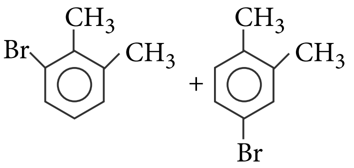
4. An organic compound X (C_4H_9Cl) on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative. Then, X is
(a) *t*-butyl chloride (b) *s*-butyl chloride
(c) *iso*-butyl chloride (d) *n*-butyl chloride.

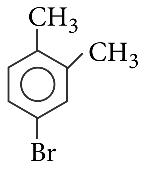
5. Addition of KI accelerates the hydrolysis of primary alkyl halides because
(a) KI is soluble in organic solvents
(b) I^- is a strong base
(c) I^- is a weak base and a poor leaving group
(d) I^- is a powerful nucleophile as well as a good leaving group.

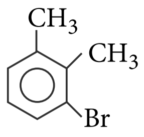
6. Which one of the following methods is used to prepare Me_3COEt in a good yield?
(a) Mixing EtONa with Me_3CCl
(b) Mixing Me_3CONa with EtCl
(c) Heating a mixture of EtOH and Me_3COH (1 : 1) in presence of conc. H_2SO_4
(d) Treatment of Me_3COH with EtMgI

7. Which of the following products is obtained when *o*-xylene is treated with Br_2 in the presence of iron?

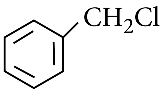
(a)


(b)


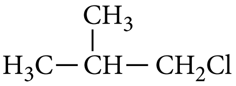
(c)


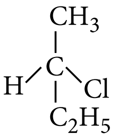
(d)


8. Which of the following compounds will undergo racemisation when solution is hydrolysed with KOH?

(i)


(ii) $CH_3CH_2CH_2Cl$

(iii)

$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2Cl$

(iv)


(a) Only (i) and (ii) (b) Only (ii) and (iv)
(c) Only (iii) and (iv) (d) Only (iv)

9. The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with
(a) PCl_5
(b) $SOCl_2$ in presence of pyridine
(c) PCl_3
(d) dry HCl in presence of anhydrous $ZnCl_2$.

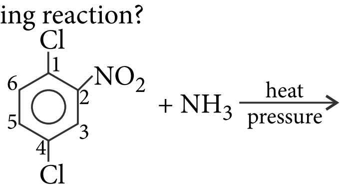
10. Mg reacts with alkyl bromide best in
(a) $C_6H_5OCH_3$ (b) $C_6H_5N(CH_3)_2$
(c) $C_2H_5OC_2H_5$
(d) equally in all three solvents.

SECTION - II

More than One Options Correct Type

11. Consider the following reaction :
$X \xrightarrow{I_2, NaOH}$ Iodoform + Sodium succinate, X can be
(a) pentan-2-one (b) acetophenone
(c) hexane-2, 5-dione (d) 4-ketopentanoic acid.

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



(a) No reaction is possible because —Cl is linked to benzene ring.
(b) A nucleophilic substitution will take place in which both —Cl will be replaced by two $—NH_2$ groups.
(c) A nucleophilic substitution will take place in which only —Cl attached to C_1 will be replaced by $—NH_2$.
(d) A nucleophilic substitution will take place in which only —Cl attached to C_4 will be replaced by $—NH_2$.

13. Which compounds among the following gives a positive iodoform test?
(a) Ethanol (b) Phenylethanal
(c) 1-Butanol (d) 2-Butanol

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

The reactions of Cl_2 gas with cold-dilute and hot concentrated NaOH give sodium salts of two different oxoacids of chlorine, P and Q, respectively. The Cl_2 gas reacts with SO_2 gas, in presence of charcoal, to give a product R. R reacts with white phosphorus to give a compound S. On hydrolysis, S gives an oxoacid T of phosphorus.

14. P and Q, respectively, are the sodium salts of
(a) hypochlorous and chloric acids
(b) hypochlorous and chlorous acids
(c) chloric and perchloric acids
(d) chloric and hypochlorous acids.

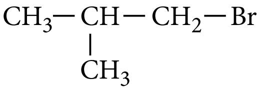
15. R, S and T, respectively, are
(a) SO_2Cl_2, PCl_5 and H_3PO_4
(b) SO_2Cl_2, PCl_3 and H_3PO_3
(c) $SOCl_2$, PCl_3 and H_3PO_2
(d) $SOCl_2$, PCl_5 and H_3PO_4

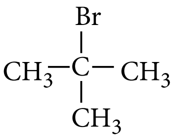
Paragraph for Questions 16 and 17

1° Alkyl halide with molecular formula C_4H_9Br (*A*) with alcoholic KOH gives (*B*) which adds HBr to give (*C*). (*C*) is an isomer of (*A*). (*A*) reacts with Na-metal in dry ether to give (*D*) which is not *n*-octane, but on treating (*A*) with Mg in dry ether followed by reaction with ethyl alcohol gives an alkane (*E*) which gives only one of the main products during photobromination. It is known that relative rate of abstraction of H-atoms from 1°, 2° and 3° carbon atoms are in the ratio of 1 : 82 : 1600.

16. Structure of 1° alkyl halide (*A*) is

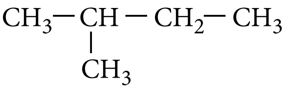
(a) $CH_3-CH_2-CH_2-CH_2-Br$

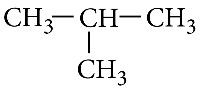
(b) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-Br$

(c) 
$CH_3-\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

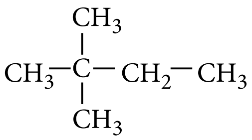
(d) none of these.

17. Structure of (*E*) is

(a) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

(b) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3$

(c) $CH_3-CH_2-CH_3$

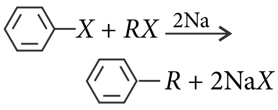
(d) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3$

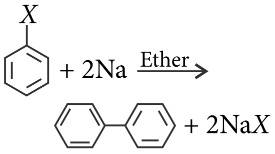
SECTION - IV

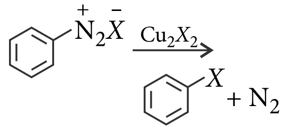
Matching List Type

18. Match the reactions given in List I with the names given in List II and select the correct answer using the codes given below the lists :

List I | **List II**

(A)  (p) Fittig reaction

(B)  (q) Wurtz-Fittig reaction

(C)  (r) Finkelstein reaction

(D) $C_2H_5Cl + NaI \xrightarrow{\text{Dry acetone}} C_2H_5I + NaCl$ (s) Sandmeyer reaction

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

(c) A-p; B-q, C-s; D-r (d) A-q; B-p; C-r; D-s

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

List I (Reactants)	**List II (Alkyl halides)**
1. $CH_3(CH_2)_3OH \xrightarrow{NaBr,\ H_2SO_4,\Delta}$	A. $CH_3CHBr(CH_2)_2CH_3$
2. $(CH_3)_3COH \xrightarrow[\text{Room temp.}]{\text{Conc. HCl}}$	B. Me_2CHCH_2Cl
3. $CH_3CH(OH)(CH_2)_2CH_3 \xrightarrow{PBr_3}$	C. $(CH_3)_3CCl$
4. $Me_2CHCH_2OH \xrightarrow{SOCl_2}$	D. $CH_3(CH_2)_3Br$

	1	2	3	4
(a)	C	D	B	A
(b)	C	D	A	B
(c)	D	C	A	B
(d)	D	C	B	A

SECTION - V

Assertion Reason Type

20. Assertion : The boiling points of alkyl halides decrease in the order: *RI* > *RBr* > *RCl* > *RF*

Reason : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

21. Assertion : Grignard reagents are prepared in ethers but not in benzene.

Reason: Grignard reagents are soluble in benzene.

22. Assertion : 3-Methylbutan-2-ol with HCl gives rearranged product.

Reason : Rearrangement is not possible in this reaction.

SECTION - VI

Integer Value Correct Type

23. An excess of methyl magnesium iodide reacts with 0.6 g of an organic compound $C_3H_6O_3$ to evolve 295.7 mL of methane gas at S.T.P. The number of active hydrogen atoms in the molecule of the organic compound is

24 Total number of compounds among the following which have zero dipole moment is

CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl, *o*-, *m*-and *p*-dichlorobenzene, benzyl chloride, benzal chloride and benzotrichloride.

25. How many of the following alkyl halides would react by S_N1 mechanism?

$CH_3Br, CH_3CH_2Br, CH_3CH_2CH_2I, (CH_3)_3CBr, BrCH_2CH{=}CH_2, C_6H_5CH_2Br, (CH_3)_3CCH_2Br, C_6H_5CHBrCH_3, CH_3CH{=}CHCH_2Cl$

SOLUTIONS

SOLUTIONS

1. **(d):** As temperature of the phases is same, their average K.E. is same.

2. **(a) :** Vapour pressure of solution (*p*)

$$= 80\% \text{ of } p_A^\circ = 0.8\, p_A^\circ$$

Let the mass of solute be *w* g.

∴ Moles of solute :

$$n_B = \frac{w_B}{M_B} = \frac{w\text{ g}}{40\text{ g mol}^{-1}} = \frac{w}{40}\text{mol}$$

Moles of octane :

$$n_A = \frac{w_A}{M_A} = \frac{114\text{ g}}{114\text{ g mol}^{-1}} = 1\text{ mol}$$

$$\text{Now, } \frac{\Delta p}{p} = \frac{n_B}{n_A} \Rightarrow \frac{p_A^\circ - 0.8\,p_A^\circ}{0.8\,p_A^\circ} = \frac{w/40}{1}$$

$$\text{or} \quad w = \frac{0.2\times 40}{0.8} = 10\text{ g}$$

3. **(d)** **4.** **(a)**

5. **(b):** Greater the effective molarity ($i \times C$), higher is the ΔT_f value and lower is the freezing point.

6. **(c) :** Mass of water (w_B) = 46 g

$$\therefore \text{ Moles of } H_2O\ (n_B) = \frac{46\text{ g}}{18\text{ g mol}^{-1}} = 2.55\text{ mol}$$

Mass of solution = 66 + 46 = 112 g

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

$$= \frac{112\text{ g}}{0.926\text{ g cm}^{-3}} = 120.95\text{ cm}^3$$

$$= 120.95 \times 10^{-3}\text{ dm}^3$$

Molarity of H_2O in the solution

$$= \frac{n_B}{V(\text{dm}^3)} = \frac{2.55}{120.95\times 10^{-3}} = 21.08\text{ M}$$

7. **(c)**

8. **(c) :** $p_A^\circ = 70$ mm of Hg, $p = 84$ mm of Hg, $x_A = 0.8$

∴ $x_B = 1 - 0.8 = 0.2$

According to Raoult's law,

$$p = p_A^\circ{\cdot}x_A + p_B^\circ{\cdot}x_B$$

$$84 = 0.8 \times 70 + 0.2 \times p_B^\circ$$

$$84 - 56 = 0.2\, p_B^\circ$$

$$\therefore \quad p_B^\circ = \frac{28}{0.2} = 140\text{ mm of Hg}$$

9. **(b):** $\pi = CRT$

$$\text{In the first case, } C = \frac{\frac{36}{180}}{1} = \frac{1}{5}\text{M}$$

$$\therefore \quad \pi = \frac{1}{5}R\times 300 = 60\,R$$

Or, 4.98 = 60 *R* …(i)

In the second case;

Let the concentration of glucose solution be *x* M.

$1.52 = x \times R \times 300$ …(ii)

Dividing equation (ii) by (i), we get

$$\frac{1.52}{4.98} = \frac{x\times R\times 300}{60R}$$

$$x = 0.061\text{ M}$$

10. **(a) :** $K_H = 4.27 \times 10^5$ mm Hg

$p = 760$ mm Hg

Applying Henry's law,

$$p = K_H x$$

$$\therefore \quad x = \frac{p}{K_H} = \frac{760}{4.27\times 10^5} = 1.78\times 10^{-3}$$

i.e., mole fraction of methane in benzene

$$= 1.78 \times 10^{-3}$$

11. **(b,c,d)**

12. (a,d) : $p = p_1^\circ x_1 + p_2^\circ x_2$

This shows that curves (*a*) and (*d*) are possible depending upon, which component is more volatile.

13. (a,c): Osmotic pressure, $\pi = CRT$

$$C_{(\text{urea})} = 6 \text{ g/100 mL} \Rightarrow 60 \text{ g/L}$$

$$\pi_{(\text{urea})} = \frac{60}{60} RT = RT$$

(a) $C_{(\text{glucose})} = 18 \text{ g/100 mL} \Rightarrow 180 \text{ g/L}$

$$\pi_{(\text{glucose})} = \frac{180}{180} RT = RT$$

(b) $\pi_{(BaCl_2)} = 3 \times 0.5\, RT = 1.5\, RT\ (i = 3)$

(c) $\pi_{(\text{sucrose})} = 1\, RT = RT$

(d) $\pi_{(\text{acetic acid})} = 2 \times 1 \times RT = 2\, RT\ (i = 2)$

14. (d): Initial amount of benzene taken

$$= 0.9 \times 78 = 70.2 \text{ g}$$

$p^\circ = 760$ mm Hg at boiling point (353 K)

$$\frac{p^\circ - p_s}{p_s} = \frac{w_A \times M_B}{M_A \times w_B}$$

$$\Rightarrow \frac{760 - 670}{670} = \frac{0.1 \times 78}{w_B} \Rightarrow w_B = 58.06 \text{ g}$$

Hence, amount of benzene frozen out

$$= 70.02 - 58.06 = 12.14 \text{ g}$$

15. (c) : $l_f = \dfrac{\Delta_f H}{M_B} = \dfrac{10.67 \times 10^3}{78} = 136.8 \text{ J/g}$

$$\text{Now, } K_f = \frac{RT_f^2}{1000 \times l_f} = \frac{8.314 \times (278.5)^2}{1000 \times 136.8}$$

We know, $\Delta T_f = K_f \times m$

$$= \frac{8.314 \times (278.5)^2}{1000 \times 136.8} \times \frac{0.1 \times 1000}{58.06} \approx 8.12 \text{ K}$$

Thus original solution must have been cooled to $= 278.5 - 8.12 = 270.38 \text{ K} \approx 270.4 \text{ K}$

16. (b): From the given data, we have

$w_B = 0.5 \times 10^{-3}$ kg [0.5% solution]

$w_A = 99.5 \times 10^{-3}$ kg

[solvent is water, density = 1000 kg/m^3]

$\Delta T_f = 273 - 272.76 = 0.24$ K

$K_f = 1.86$ K kg mol^{-1}

$$\therefore\ M = \frac{1000 \times K_f \times w_B}{\Delta T_f \times w_A}$$

$$= \frac{1000 \times 1.86 \times 0.5 \times 10^{-3}}{0.24 \times 99.5 \times 10^{-3}} = 38.94 \text{ g mol}^{-1}$$

∴ The apparent molar mass of KCl = 38.94 g mol^{-1}

The molar mass of KCl = 39 + 35.5 = 74.5 g mol^{-1}

$$\therefore\ i = \frac{\text{Normal molar mass}}{\text{Apparent molar mass}}$$

$$= \frac{74.5}{38.94} = 1.91 \approx 2$$

17. (c) : In solution, KCl dissociates as follows :

$KCl \longrightarrow K^+ + Cl^-$

If α is degree of dissociation, then

	$KCl \rightleftharpoons$	K^+ +	Cl^-
Initial moles	1	0	0
Moles after dissociation	(1 – α)	α	α

The number of moles after dissociation

$$= 1 - \alpha + \alpha + \alpha = (1 + \alpha)$$

$$\therefore\ i = \frac{1 + \alpha}{1} \text{ or } \alpha = i - 1$$

= 1.92 – 1 [∵ i = 1.92]

= 0.92 or 92%

18. (d)

19. (d): (A) Molarity $= \dfrac{10 \cdot 6}{106} \times \dfrac{1000}{100} = 1 \text{ M}$

(B) Molarity $= \dfrac{34.2 \text{ g L}^{-1}}{342 \text{ g mol}^{-1}} = 0.1 \text{ M}$

(C) 9.8% H_2SO_4 means 9.8 g of H_2SO_4 in 100 g of solution. Volume of solution = 100/1.25 = 80 mL

$$\text{Molarity} = \frac{9.8}{98} \times \frac{1}{80} \times 1000 = 1.25 \text{ M}$$

(D) 20% of ethanol solution means 20 cc of ethanol in 100 cc of solution.

Mass of solution = 100 × 0.938 = 93.8 g

Volume of water = 80 cc

Mass of water = 80 g

Mass of 20 cc ethanol = 93.8 – 80 = 13.8 g

$$\text{Molarity} = \frac{13.8}{46} \times \frac{1}{100} \times 1000 = 3.0 \text{ M}$$

20. (b): Raoult's law is a special case of Henry's law. The two laws differ in the proportionality constant. In Raoult's law, it is equal to vapour pressure of pure component (p°). While in Henry's law, it is equal to experimentally determined value of Henry's constant (K_H).

21. (a)

22. (d): If red blood cells are removed from the body and placed in pure water, water enters the cell and pressure inside the cell increases. As water enters, concentration of the salt content in the cells decreases.

23. **(4) :** $n_{Na^+} = \dfrac{92\text{ g}}{23\text{ g mol}^{-1}} = 4\text{ mol}$

$$\text{Molality} = \frac{n_{Na^+}}{w_{H_2O}(\text{in kg})} = \frac{4}{1} = 4\text{ m}$$

24. **(2) :** Moles of ethylene glycol

$$= \frac{45\text{ g}}{62\text{ g mol}^{-1}} = 0.73\text{ mol}$$

$$\text{Mass of water in kg} = \frac{650}{1000} = 0.65\text{ kg}$$

$$\text{Molality} = \frac{\text{Moles of ethylene glycol}}{\text{Mass of water (in kg)}}$$

$$= \frac{0.73\text{ mol}}{0.65\text{ kg}} = 1.12\text{ mol kg}^{-1}$$

Therefore, freezing point depression,
$\Delta T_f = 1.86\text{ K kg mol}^{-1} \times 1.12\text{ mol kg}^{-1} = 2.08\text{ K} \approx 2\text{ K}$

25. **(4) :** After mixing, total volume of the solution = 200 mL
Conc. of urea in the solution = 1.4 × 1000/200

$$= 7.0\text{ g L}^{-1} = \frac{7.0}{60}\text{ mol L}^{-1}$$

$$\pi_{(\text{urea})} = CRT = \frac{7.0}{60} \times 0.0821 \times 293 = 2.80\text{ atm}$$

Conc. of cane sugar in the solution = 3·42 × 1000/200

$$= 17.10\text{ g L}^{-1} \Rightarrow \frac{17.10}{342}\text{ mol L}^{-1}$$

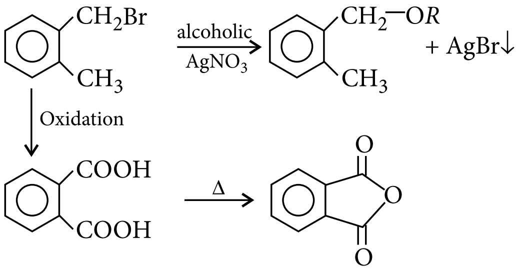
$$\pi_{(\text{cane sugar})} = CRT = \frac{17.10}{342} \times 0.0821 \times 293 = 1.20\text{ atm}$$

∴ Total osmotic pressure = 2.80 + 1.20 atm
= 4.0 atm

HALOALKANES AND HALOARENES

1. **(a) :** Density increases as molecular mass increases *i.e.*, (i) < (ii) < (iii) < (iv).

2. **(d) :**



(Phthalic anhydride)

3. **(c) :** Compound in option (c) has all equitorial substituents, hence, it is most stable and undergoes elimination with slowest rate.

4. **(a) :** $2CH_3C(CH_3)_2Cl + 2Na \xrightarrow[-2NaCl]{\text{Diethyl ether}}$

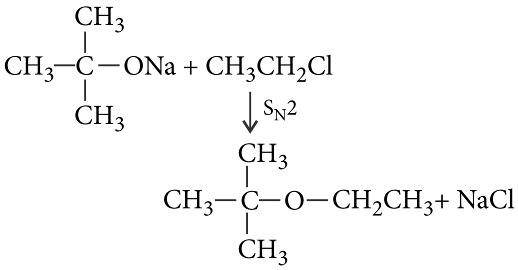
$CH_3C(CH_3)_2C(CH_3)_2CH_3$

$CH_3C(CH_3)_2C(CH_3)_2CH_3 + Cl_2 \xrightarrow[-2HCl]{h\upsilon}$

$CH_3C(CH_3)_2C(CH_3)_2CH_2Cl$
1-Chloro-2, 2, 3, 3-tetramethylbutane

5. **(d) :** I^- is a powerful nucleophile as well as a good leaving group.

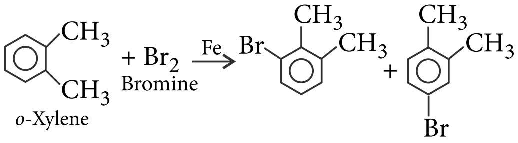
6. **(b) :**



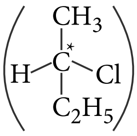
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-ONa + CH_3CH_2Cl \xrightarrow{S_N2} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-O-CH_2CH_3 + NaCl$$

Williamson synthesis (S_N2) is given by 1° alkyl halides.

7. **(b) :**



8. **(d) :** Due to chirality, only compound (iv)

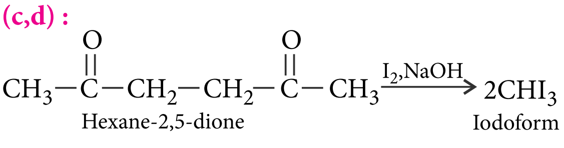


will undergo racemisation.

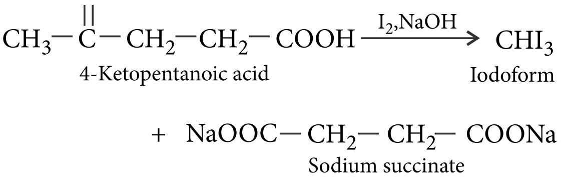
9. **(b)**

10. **(c) :** As Grignard reagent can be prepared in all the three solvents but $C_2H_5OC_2H_5$ is probably the best, since lone pair of electrons on O-atom in $C_6H_5OCH_3$ and N-atom in $C_6H_5N(CH_3)_2$ are partly delocalized over the benzene ring and hence, are less available than lone pair of electrons on oxygen in $C_2H_5OC_2H_5$ for coordination.

11. **(c,d) :**



$$\underset{\text{Hexane-2,5-dione}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \xrightarrow{I_2,NaOH} \underset{\text{Iodoform}}{2CHI_3} + \underset{\text{Sodium succinate}}{NaOOC-CH_2-CH_2-COONa}$$



$$\underset{\text{4-Ketopentanoic acid}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_2-COOH} \xrightarrow{I_2,NaOH} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium succinate}}{NaOOC-CH_2-CH_2-COONa}$$

Compounds having $CH_3-\underset{\underset{O}{\|}}{C}-$ group give iodoform test.

12. (a,b,d) : The —Cl group present at the *o*- and *p*-positions to the electron withdrawing group is activated towards nucleophilic substitution reaction, hence, only —Cl present at the *o*-and/or *p*-position to the $—NO_2$ group will be replaced by nucleophile.

13. (a,d) : Iodoform reaction is given by compounds which contain either $CH_3-\underset{\underset{O}{\|}}{C}-$ group or $CH_3-\overset{\overset{OH}{|}}{CH}-$ group.

14. (a) : $\underset{\text{(cold and dil.)}}{Cl_2 + 2NaOH} \longrightarrow \underset{\text{Sodium hypochlorite}}{NaOCl} + H_2O + NaCl$

$\underset{\text{(hot and conc.)}}{3Cl_2 + 6NaOH} \longrightarrow \underset{\text{Sodium chlorate}}{NaClO_3} + 5NaCl + 3H_2O$

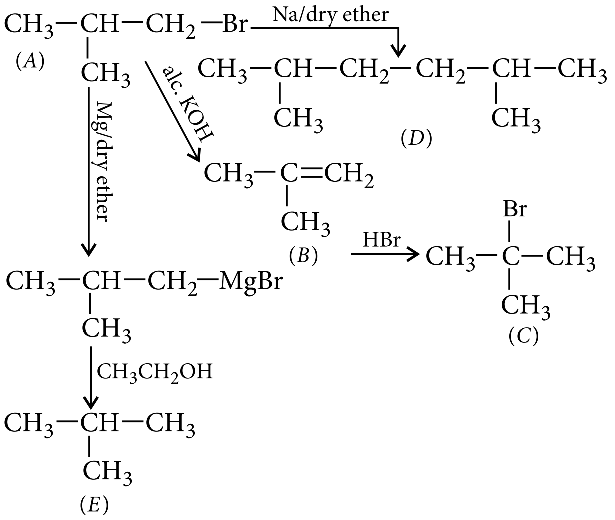
NaOCl is salt of hypochlorous acid (*P*).
$NaClO_3$ is salt of chloric acid (*Q*).

15. (a) : $Cl_2 + SO_2 \xrightarrow{\text{Charcoal}} SO_2Cl_2(R)$

$10SO_2Cl_2 + P_4 \longrightarrow 4\,PCl_5(S) + 10SO_2$

$PCl_5 + 4H_2O \longrightarrow H_3PO_4(T) + 5HCl$

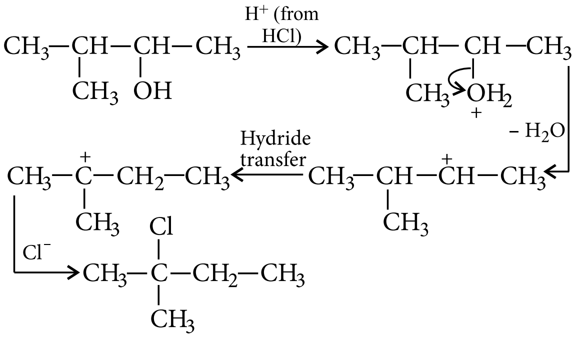
16. (b) :



17. (b) **18. (b)** **19. (c)** **20. (b)**

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

22. (c) : Reaction of hydrogen halide with alcohol proceeds via the carbocation formation hence, alkyl halide corresponding to most stable carbocation is formed.



Rearranged product

23. (2): Molecular mass of $C_3H_6O_3$
$= 3 \times 12 + 6 \times 1 + 3 \times 16 = 90$

∴ 1 mol of $C_3H_6O_3$ = 90 g

Now 0.6 g of the compound at S.T.P. evolves
$= 295.7$ mL CH_4

∴ 90 g of the compound at S.T.P. will evolve

$$= \frac{295.7}{0.6} \times 90 = 44355 \text{ mL } CH_4$$

$$\text{Moles of } CH_4 \text{ produced} = \frac{44355}{22400} = 1.98 \approx 2$$

∴ 1 mol of compound produces 2 mol of CH_4.

∴ There are two active hydrogen atoms present in one molecule of compound.

24. (2): CCl_4 and *p*-dichlorobenzene will have zero dipole moment.

25. (5): Only 3°, allyl and benzyl halides react by S_N1 mechanism. These are : $(CH_3)_3CBr$, $BrCH_2CH = CH_2$, $C_6H_5CH_2Br$, $C_6H_5CHBrCH_3$ and $CH_3CH = CHCH_2Cl$.

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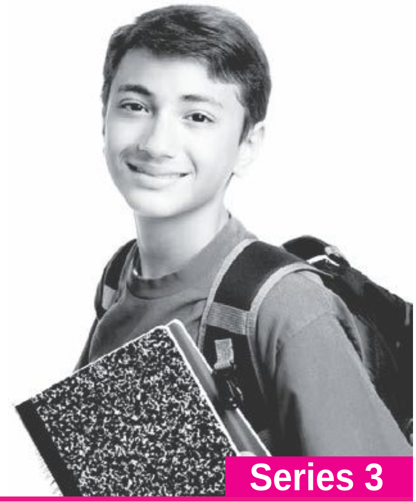
ACE YOUR WAY CBSE XII



Series 3

CHAPTERWISE PRACTICE PAPER : GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS | *p*- BLOCK ELEMENTS (GROUP 15 to 18)

Time Allowed : 3 hours Maximum Marks : 70

GENERAL INSTRUCTIONS

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

1. Copper and silver lie below in the electrochemical series and yet they are found in the combined state as sulphides in nature. Explain.

2. Why do noble gases form compounds with fluorine and oxygen only?

3. What is benefaction?

4. Iodine forms, I_3^- ion but F_2 does not form F_3^- ion. Why?

5. What is the role of cryolite in the metallurgy of aluminium?

6. List two uses of each neon and argon gases.

7. What are depressants? How would you separate zinc sulphide (ZnS) and lead sulphide (PbS) ores?

8. Describe the chemical reaction of chlorine with
(i) dry calcium hydroxide (slaked lime).
(ii) aqueous solution of hot calcium hydroxide (milk of lime).

OR

Explain :

(i) SF_6 is known but SCl_6 is not.
(ii) SF_6 is inert towards hydrolysis.

9. Free energies of formation ($\Delta_f G$) of $MgO_{(s)}$ and $CO_{(g)}$ at 1273 K and 2273 K are given below:

$\Delta_f G\ (MgO_{(s)}) = -\ 941$ kJ/mol at 1273 K
$\Delta_f G\ (MgO_{(s)}) = -\ 314$ kJ/mol at 2273 K
$\Delta_f G\ (CO_{(g)}) = -\ 439$ kJ/mol at 1273 K
$\Delta_f G\ (CO_{(g)}) = -\ 628$ kJ/mol at 2273 K

On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for $MgO_{(s)}$.

10. Give the formula of :
(i) Polyphosphoric acid
(ii) Polymetaphosphoric acid
(iii) Sodium triphosphate
(iv) Trimetaphosphate

11. (i) Which of the following metals cannot be extracted by the smelting process?
Al, Zn, Fe and Pb
(ii) How is leaching carried out in case of low grade copper ores?
(iii) Give a method for separation of nickel from cobalt.

12. Explain

(i) Why NH_3 is basic while BiH_3 is only feebly basic?

(ii) Nitrogen exists as diatomic molecule and phosphorus as P_4, why?

13. (i) Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reducing?

(ii) Out of C and CO which is a better reducing agent

(a) at 673 K?

(b) for ZnO?

14. Give reason :

(i) Xenon does not form fluorides such as XeF_3 and XeF_5.

(ii) Out of nobles gases, xenon is known to form established chemical compounds.

(iii) Noble gases have very low boiling points.

15. Name the chief ores of tin, iron and aluminium. What methods are employed for the concentration of their ores? Explain one in brief.

16. *A* is a binary compound of univalent metal. 1.422 g of *A* reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid, *B*, that forms a hydrated double salt, *C*, with $Al_2(SO_4)_3$. Identify *A*, *B* and *C*.

17. Explain :

(i) Zone refining.

(ii) Column chromatography.

18. (i) Which form of sulphur shows paramagnetic behaviour?

(ii) Compounds of fluorine and oxygen are called fluorides and not oxides. Explain.

(iii) Sulphur disappears when boiled with an aqueous solution of sodium sulphite. Why?

19. Which method would you suggest for the separation of the metals in the following mixtures?

(i) Zinc and iron

(ii) Copper and magnesium

(iii) Rare earths

Given reasons for your choice.

OR

Describe the role of

(i) NaCN in the extraction of gold from gold ore.

(ii) SiO_2 in the extraction of copper from copper matte.

20. Two elements of the same group combine to form the compounds of the type AA', AA'_3 and AA'_5.

(i) Draw the structure of each type, showing number of lone pairs and bond pairs.

(ii) With which group, these elements belong? And what name is given to these compounds?

(iii) Calculate the oxidation state of *A* in each case.

21. (i) When the ore haematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel but also produces a silicate slag, that is useful in making building material such as cement. Discuss the same and show through balanced chemical equations.

(ii) What type of chemical processes oxidation, reduction, etc., are involved during the production of steel from haematite?

(iii) Which one is a good reducing agent (C or CO) for Fe_2O_3, below 1073 K?

22. Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

23. Two friends Riya and Priya were playing in playground. Suddenly, first rain of the season started. Riya wanted to go into the rain but Priya stopped her giving some reason. But Riya did not listen to her and took bath in rainfall. After sometime, her body gets yellowish brown patches for which she was medicated.

(i) What reason Priya would have given her?

(ii) Why did Riya's skin get yellowish brown patches?

(iii) What do you understand by the term acid rain, how it is generated?

(iv) What values are shown by Priya?

24. Explain the following :

(i) Zinc but not copper is used for the recovery of Ag from the complex $[Ag(CN)_2]^-$.

(ii) Partial roasting of sulphide ore is done in the metallurgy of copper.

(iii) Why is chalcocite roasted and not calcined during recovery of copper?

(iv) Aluminium metal is frequently used as a reducing agent for the extraction of metals such as chromium, manganese, etc.

(v) Magnesium oxide is used for the lining in steel furnace.

OR

Answer the following questions briefly :

(i) What is the actual reducing agent of haematite in blast furnace?

(ii) Give the equations for the recovery of lead from galena.

(iii) Why is sodium chloride added during electrolysis of fused anhydrous magnesium chloride.

(iv) Write the overall reaction taking place in the process used for the electrolysis of alumina by Hall-Heroult process.

(v) Mention two important substances present in the 'anode mud' obtained in the electrorefining of copper.

25. What happens when

(i) Gold is treated with aqua-regia?

(ii) Calcium phosphate is heated with a mixture of sand and carbon?

(iii) Phosphorus reacts with nitric acid?

(iv) Zinc is treated with very dilute nitric acid?

(v) Iodine reacts with concentrated nitric acid?

OR

(i) Give the formula and describe the structure of a noble gas species which is isostructural with:

(a) ICl_4^- (b) BrO_3^-

(ii) Does the hydrolysis of XeF_6 lead to a redox reaction?

(iii) What happens when Cl_2 reacts with hot concentration solution of sodium hydroxide? Is this reaction a disproportionation reaction?

26. (i) Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.

(ii) Write chemical reactions taking place in the extraction of zinc from zinc blende.

OR

(i) At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why ?

(ii) Why is it advantageous to roast sulphide ore to the oxide before reduction ?

(iii) Name the chief ore of silver. Describe with chemical equations the extration of silver from this ore.

SOLUTIONS

1. Due to high polarising power of Cu and Ag ions, their sulphides are even more stable than the metals.

2. Both fluorine and oxygen are most electronegative elements, they can promote electrons from filled orbitals of noble gases to vacant *d*-orbitals.

3. The process of removal of gangue or matrix from the ore is called benefaction.

4. I atoms have vacant *d*-orbitals therefore, I_2 accepts electrons from I^- ion to form I_3^-, whereas F atoms do not have vacant *d*-orbital, therefore F_2 cannot accept electrons from F^- to form F_3^- ion.

5. The role of cryolite is as follows :

(i) It makes alumina a good conductor of electricity.

(ii) It lowers the melting point of the mixture from 2323 K to about 1140 K.

6. Uses of neon :

(i) It is used in discharge tubes and fluorescent bulbs for advertising purposes.

(ii) Neon bulbs are used in botanical gardens and in green houses.

Uses of argon :

(i) It is used in filling incandescent and fluorescent lamps where its presence retards the sublimation of the filament and thus increases the life of the lamp.

(ii) It is also used in "neon signs" for obtaining lights of different colours.

7. Depressants are the chemicals which are used for preventing one type of sulphide ore particles from forming the froth. Zinc sulphide ore can be separated from lead sulphide ore by froth floatation process using sodium cyanide (NaCN) as depressant. Sodium cyanide acts as depressant for ZnS but does not prevent PbS from the formation of froth. Thus, ZnS can be separated from PbS.

8. (i)

$$\underset{\text{Slaked lime}}{2Ca(OH)_2} + 2Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{Ca(OCl)_2} + 2H_2O + CaCl_2$$

(ii)

$$\underset{\text{Milk of lime}}{6Ca(OH)_{2(aq)}} + 6Cl_2 \longrightarrow 5CaCl_2 + \underset{\text{Calcium chlorate}}{Ca(ClO_3)_2} + 6H_2O$$

OR

(i) Fluorine atom is smaller in size, so six F^- ions can surround a sulphur atom. The case is not so with chlorine atom due to its large size. So, SF_6 is known but SCl_6 is not known due to interionic repulsion between larger Cl^- ions.

(ii) In SF_6, the six F atoms sterically protect the sulphur atom by the attack of water molecules due to steric hindrance. Further, F atom does not have vacant *d*-orbitals to accept the electrons donated by H_2O molecules. As a result, SF_6 does not undergo hydrolysis.

9. At 1273 K and 2273 K,

(i) $Mg_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow MgO_{(s)}$

(ii) $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}$

On subtracting eq. (i) from (ii),

$MgO_{(s)} + C_{(s)} \longrightarrow Mg_{(s)} + CO_{(g)}$

Now,

$\Delta_r G = \Delta_f G\,(CO) - \Delta_f G\,(MgO)$

At 1273 K, $\Delta_r G = -439 - (-941)$ kJ/mol

$= +502$ kJ/mol

At 2273 K, $\Delta_r G = -628 - (-314)$ kJ/mol

$= -314$ kJ/mol

As $\Delta_r G$ in negative at 2273 K. Thus, carbon can act as reducing agent at 2273 K.

10. **(i)** $H_{n+2}P_nO_{3n+1}$ **(ii)** $(HPO_3)_n$

(iii) $Na_5P_3O_{10}$ **(iv)** $Na_3P_3O_9$

11. **(i)** Aluminium cannot be extracted by the smelting process because

(a) Al is highly electropositive element, having strong affinity for oxygen. Hence, Al_2O_3 is very stable compound. So, it can not be reduced by carbon.

(b) Al_2O_3 on heating with carbon forms aluminium carbide (Al_4C_3).

$2Al_2O_3 + 9C \longrightarrow Al_4C_3 + 6CO$

(ii) The leaching of the low grade copper ores is carried out with acids in the presence of air when copper goes into solution as Cu^{2+} ions. Therefore,

$2Cu_{(s)} + 2H_2SO_{4(aq)} + O_{2(g)} \longrightarrow 2CuSO_{4(aq)} + 2H_2O_{(l)}$

or $Cu_{(s)} + 2H^+_{(aq)} + 1/2O_{2(g)} \longrightarrow Cu^{2+}_{(aq)} + H_2O_{(l)}$

(iii) Nickel (Ni) can be separated from cobalt (Co) by Mond's process. CO is passed over a heated mixture of Ni and Co at 330–350 K, Ni forms volatile $Ni(CO)_4$ but Co does not. The volatile $Ni(CO)_4$ is separated and then heated at 450–470 K to get pure Ni.

$$\underset{\text{Impure nickel}}{Ni + 4CO} \xrightarrow{330\text{-}350\ K} \underset{\text{Nickel tetracarbonyl}}{Ni(CO)_4} \xrightarrow{450\text{-}470\ K} \underset{\text{Pure nickel}}{Ni + 4CO}$$

12. **(i)** NH_3 is strongly basic because it can easily donate its electron pair due to small size of nitrogen atom as a result of which electron density is concentrated over a small region. BiH_3, on the contrary is feebly basic because of its larger size. Due to increase in size the electron density gets diffused over a larger region and hence, the ability to donate the electron pair decreases.

(ii) Nitrogen exists as a diatomic molecule (N_2) due to small size of nitrogen atom and absence of vacant *d*-orbitals in its valence shell it has strong ability to form multiple bond ($N \equiv N$). The other members of group-15 *i.e.*, phosphorus, arsenic and antimony all exists as discrete tetra-atomic tetrahedral molecules, *viz*, P_4, As_4, and Sb_4 because these are not capable of forming multiple bonds due to their bigger size and repulsions between non-bonded electrons of the inner core.

13. **(i)** The entropy of a substance is higher in liquid state than in solid state. In the reduction of a metal oxide, the entropy change (ΔS) will be +ve if the metal formed is in liquid state. Thus, the value of $\Delta G°$ becomes negative and reduction occurs easily.

(ii) (a) When carbon acts as a reducing agent, it is either converted into CO or CO_2 or both.

$2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)}$

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

CO is oxidised to CO_2 when it is used as a reducing agent.

$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$

From the Ellingham diagram, it is clear that at temperature 673 K, the $\Delta G°$ of formation of CO_2 from CO is more negative than the formation of CO or CO_2 from carbon. Hence, at temperature 673 K, CO is better reducing agent than C.

(b) From the Ellingham diagram, it is clear that the free energy formation of CO from C is lower at temperatures above 1120 K while free energy of formation of CO_2 from carbon is lower above 1323 K than the free energy of formation of ZnO. However, the free energy formation of CO_2 from CO is always higher than that of ZnO. Hence, C is better reducing agent for ZnO.

14. (i) All the filled orbitals of Xe have paired electrons. The promotion of one, two or three electrons from the 5*p*-filled orbitals to the 5*d*-vacant orbitals will give rise to two, four and six half-filled orbitals, respectively. Therefore, Xe can combine with even number of F-atoms but not odd. Thus, it cannot form XeF_3 and XeF_5.

(ii) Except radon which is radioactive, Xe has the least ionization energy among noble gases and hence, it readily forms chemical compounds with strong oxidising agent like O_2 and F_2.

(iii) Noble gases are monoatomic. Their atoms are held together by weak dispersion forces and hence, can be liquefied at very low temperature. So, they have low boiling points.

15. Chief ores of

Tin: cassiterite, SnO_2

Iron: haematite, Fe_2O_3, magnetite, Fe_3O_4

Aluminium: bauxite, $Al_2O_3.2H_2O$

Diaspore, $Al_2O_3.H_2O$.

(i) **Concentration of cassiterite :** It is concentrated by gravity separation process.

(ii) **Concentration of haematite :** The ore is crushed and washed with water to remove siliceous impurities. The washed ore is then dressed up by electromagnetic separation.

(iii) **Concentration of bauxite :** The ore is concentrated by Baeyer's process. The crushed ore is digested with concentrated solution of sodium hydroxide in which aluminium oxide dissolves forming soluble sodium meta-aluminate ($NaAlO_2$) while impurities remains insoluble and settle down.

$$Al_2O_3.2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2O$$

The filtrate containing sodium meta-aluminate is agitated with freshly precipitated $Al(OH)_3$ when sodium meta-aluminate undergoes hydrolysis to precipitate $Al(OH)_3$.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + \underset{\text{ppt.}}{Al(OH)_3\downarrow}$$

The precipitate is washed, dried and heated to get Al_2O_3.

$$2Al(OH)_3 \xrightarrow[1500°C]{\Delta} Al_2O_3 + 3H_2O$$

16. As the solid *B* forms a hydrated double salt with $Al_2(SO_4)_3$, it should be a sulphate of a univalent metal, M_2SO_4.

One molecule of sulphate contains one sulphur atom, *i.e.*, the mass of the sulphate which contains 32.1 g sulphur should be its molecular mass.

0.321 g sulphur is present in 1.422 + 0.321 = 1.743 g of *B*

32.1 g of sulphur is present in $= \dfrac{1.743}{0.321} \times 32.1$
$= 174.3$ g

Let the atomic mas of univalent metal be *x*.

$\therefore \quad M_2SO_4 = 2x + 32.1 + 64.0 = 174.3$

or $\quad 2x = 78.2$

$\quad x = 39.1$

Atomic mass 39.1 corresponds to potassium, K.

Thus, the compound *B* is K_2SO_4 and the compound *C* is $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$.

Since, *B* is formed with interaction of *A* and sulphur, *A* must be an oxide of potassium (most probably KO_2).

$$\underset{2\times 71.1}{2KO_2} + \underset{32.1}{S} \longrightarrow \underset{174.3}{K_2SO_4}$$

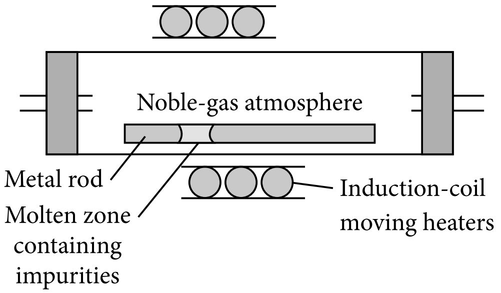
32.1 g of S reacts with $A = 2 \times 71.1$ g

0.321 g of S reacts with $A = \dfrac{2\times 71.1}{32.1} \times 0.321 = 1.422$ g

Thus, *A* is supported by the given data.

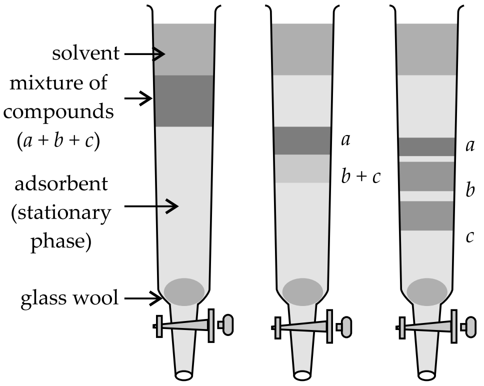
A is, therefore, potassium superoxide, KO_2.

17. (i) **Zone refining :** This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of the impure metal. The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off. This method is very useful for producing semiconductor and other metals of very high purity, *e.g.*, germanium, silicon, boron and gallium.



Zone refining process

(ii) **Column chromatography :** Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end. The mixture adsorbed on adsorbent is placed on the top of the adsorbent column.



Column chromatography, different stages of separation of components of a mixture

Later the adsorbed components are extracted (eluted) from the column with a suitable solvent (eluent). Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distance in the column.

18. (i) In vapour state, sulphur partly exists as S_2 molecules and S_2 molecule has two unpaired electrons in the antibonding π^*–molecular orbitals like O_2 and hence, S_2 exhibits paramagnetic nature.

(ii) This is because of higher electronegativity of fluorine than oxygen. In naming a compound, the electropositive or less electronegative element is taken first, thus, the compounds of fluorine and oxygen are called oxygen fluorides, not fluorine oxides.

(iii) Sulphur combines with sodium sulphite to form sodium thiosulphate which is soluble in water and hence, S disappears.

$$Na_2SO_3 + S \longrightarrow \underset{\text{Sod. thiosulphate}}{Na_2S_2O_3}$$

19. (i) **Zinc and iron :** Zinc and iron can be separated from the mixture by fractional distillation. The mixture is distilled, where zinc with low boiling point distils over, leaving behind iron.

(ii) **Copper and magnesium :** Copper and magnesium metals can be separated from the mixture by electrolytic refining. The mixture is converted into a rod and made the anode, while a thin plate of pure copper serves as the cathode. The electrolytic tank contains a solution of copper sulphate acidified with dil. H_2SO_4, which acts as a electrolyte, on passing electricity. Cu from the anode dissolve in the solution to give Cu^{2+} and thus, these Cu^{2+} ions are discharged at the cathode as pure metal.

(iii) **Rare earths :** Rare earths inlcude lanthanides and actinides. All lanthanide ions are typically trivalent M^{3+} and almost identical in size. Their chemical properties, which are determined by the size and charge of their ions, are almost identical. This renders the separation of one metal from another difficult. Different methods employed for their separation given below are based on the light differences in their solubility, stability, and basic properties. Modern methods are based on valence change and ion exchange.

(1) Ion exchange method
(This is a very effective and rapid method.)
(2) Complex formation
(3) Solvent extraction
(4) Fractional crystallisation
(5) Valency change method
(6) Thermal reaction
(7) Precipitation

OR

(i) NaCN is used for leaching of gold ore in the presence of air from which the gold is obtained later by displacement method.

$$4Au_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(l)} + O_{2(g)} \longrightarrow 4[Au(CN)_2]^-_{(aq)} + 4OH^-_{(aq)}$$

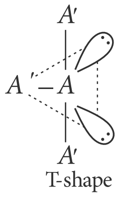
(ii) During roasting, the impurity, *i.e.*, ferrous sulphide, is oxidised to ferrous oxide which is then reacted with silica (flux) to form slag (ferrous silicate).

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$$

$$\underset{\text{Oxide}}{FeO} + \underset{\text{Flux}}{SiO_2} \longrightarrow \underset{\text{Ferrous silicate (Slag)}}{FeSiO_3}$$

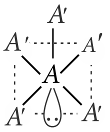
20. (i) $AA' \Rightarrow \underset{\text{Linear}}{:\overset{\cdot\cdot}{\underset{\cdot\cdot}{A}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{A'}}:}$

$AA'_3 \Rightarrow$



T-shape

$AA'_5 \Rightarrow$



Square pyramidal

(ii) These elements belong to halogen family and these compounds are called interhalogen compounds.

(iii) Let the oxidation state of A is x.

In AA' : $x + (-1) = 0 \Rightarrow x = +1$

In AA'_3 : $x + (-1)\,3 = 0 \Rightarrow x = +3$

In AA'_5 : $x + (-1)\,5 = 0 \Rightarrow x = +5$

21. (i) Haematite is an ore of iron when burns in air with coke at high temperature gives iron in a free state but also produces a silicate slag.

(a) $C + O_2 \xrightarrow{2000°C} CO + \frac{1}{2}O_2$

(b) $3CO + Fe_2O_3 \longrightarrow 2Fe + 3CO_2$

(c) $CaCO_3 \longrightarrow CaO + CO_2$

(d) $\underset{\text{Lime}}{CaO} + \underset{\text{Silica}}{SiO_2} \longrightarrow \underset{\text{Slag}}{CaSiO_3}$

(ii) In haematite, some FeO is also present along with Fe_2O_3. Thus, first of all this FeO is oxidised to Fe_2O_3 and after that the Fe_2O_3 gets reduced to Fe_3O_4 and finally to Fe.

(iii) Below 1073 K, CO is more effective, because the $\Delta G°$ value for the conversion of CO into CO_2 is more negative.

22. (i) **Electronic configurations** :

${}_{8}O = [He]2s^2\,2p^4$

${}_{16}S = [Ne]3s^2 3p^4$

${}_{34}Se = [Ar]3d^{10}4s^2 4p^4$

${}_{52}Te = [Kr]4d^{10}5s^2 5p^4$

${}_{84}Po = [Xe]4f^{14}5d^{10}6s^2\,6p^4$

All these elements have same ns^2np^4 (n = 2 to 6) valence shell electronic configuration and hence, are placed in the same group of the periodic table.

(ii) **Oxidation states :** They need two more electrons to acquire the nearest noble gas configuration. So, the minimum oxidation state of these elements should be –2. Oxygen predominantly and sulphur to some extent being electronegative, show an oxidation state of –2. Since, these elements have six electrons in the valence shell, therefore, the maximum oxidation state they can show is, + 6. Other positive oxidation states shown by these elements are +2 and +4. Although, oxygen due to the absence of *d*-orbitals does not show oxidation states of +4 and +6. Thus, on the basis of minimum and maximum oxidation states, these elements are justified to be placed in the same group *i.e.*, group–16 of the periodic table.

(iii) **Formation of hydrides :** All the elements complete their respective octets by sharing two of their valence electrons with 1*s*-orbital of hydrogen to form hydrides of the general formula EH_2 *i.e.*, H_2O, H_2S, H_2Se, H_2Te and H_2Po. Therefore, on the basis of formation of hydrides of the general formula, EH_2, these elements are justified to be placed in same group of the periodic table.

23. (i) Priya told her that first rainfall of season contains HNO_3, which is harmful.

(ii) When water containing acid comes in contact with the skin, denaturation of proteins occurs, causes yellowish brown patches.

(iii) Rain that contains high concentration of pollutants mainly sulphur dioxide and nitrogen oxide which released into the atmosphere by burning of fossil fuels *i.e.*, coal or oil. These pollutants when react with rain water produce acid rain.

(iv) Values shown by Priya are concern about her friend's health and subject knowledge.

24. (i) Zinc is more powerful reducing agent having reduction potential $(E^\circ_{Zn^{2+}/Zn} = -0.76\ V)$ lower than that of copper $(E^\circ_{Cu^{2+}/Cu} = 0.34\ V)$. Zinc is also cheaper than copper.

(ii) Partial roasting of sulphide ore forms some oxide. This oxide then reduces the remaining sulphide ore into metal.

$$2CuS + 3O_2 \longrightarrow 2CuO + 2SO_2\uparrow$$

$$2CuO + CuS \longrightarrow 3Cu + SO_2 \text{(Auto-reduction)}$$

(iii) Chalcocite (Cu_2S), is a sulphide ore. To convert this into metal oxide, oxygen is required. Therefore, it is roasted and not calcined.

(iv) Aluminium has great affinity for oxygen. It acts as a reducing agent for the metals, having high melting point, are to be extracted from their oxides.

$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$

(v) Magnesium oxide acts as a flux to remove impurities of Si, P and S through slag formation.

$$\left.\begin{array}{l} MgO + SiO_2 \rightarrow MgSiO_3 \\ 3MgO + P_2O_5 \rightarrow Mg_3(PO_4)_2 \\ MgO + SO_2 \rightarrow MgSO_3 \end{array}\right\}\text{Slag}$$

OR

(i) Carbon monoxide is the actual reducing agent of haematite in the blast furnance.

$4FeO + O_2 \longrightarrow 2Fe_2O_3$

$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$

$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$

$FeO + CO \longrightarrow Fe + CO_2$

(ii) Lead is mainly extracted from sulphide ore called galena. Roasting is done followed by reduction with carbon. Finally, self-reduction takes place.

$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$

$PbS + 2O_2 \longrightarrow PbSO_4$

$PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$

$PbS + 2PbO \longrightarrow 3Pb + SO_2$

(iii) The anhydrous magnesium chloride is fused with NaCl and anhydrous calcium chloride. The mixture is electrolysed at 700 °C in the presence of an inert gas in an elctrolytic cell. Magnesium is discharged at the cathode. The purpose of the addition of NaCl and $CaCl_2$ to anhydrous $MgCl_2$ is to lower the fusion temperature and make the fused mass a good conductor of electrcity. Sodium chloride prevents the hydrolysis of magnesium chloride.

(iv) Cathode : $Al^{3+}_{(melt)} + 3e^- \longrightarrow Al_{(l)}$

Anode : $C_{(s)} + O^{2-}_{(melt)} \longrightarrow CO_{(g)} + 2e^-$

$C_{(s)} + 2O^{2-}_{(melt)} \longrightarrow CO_{2(g)} + 4e^-$

(v) Two important substances present in the anode mud are silver and gold.

25. (i) $Au + 3HNO_3 + 4HCl \longrightarrow HAuCl_4 + 3NO_2 + 3H_2O$

(ii) $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 10CO + 6CaSiO_3$

(iii) $P_4 + 10HNO_3 + H_2O \longrightarrow 4H_3PO_4 + 5NO + 5NO_2$

(iv) $4Zn + 10\,HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$

(v) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

OR

(i) (a) Structure of ICl_4^- :

No. of electrons in valence shell of the central I atoms = 7

No. of electrons provided by four Cl atoms = 4 × 1 = 4

Charge on central atom = 1

$\therefore$ Total no. of electrons around the central atom = 7 + 4 + 1 = 12

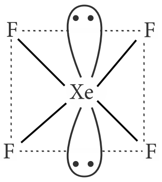
Total no. of electron pairs around the central atom $= \frac{12}{2} = 6$

But the no. of bond pairs = 4

($\because$ four I — Cl bonds)

$\therefore$ No. of lone pairs = 6 – 4 = 2

(a) Therefore, according to VSEPR theory ICl_4^- should be square planar.



Now, a noble gas compound having 12 electrons in the valence shell of the central atom is XeF_4 , with square planar structure.

(b) In BrO_3^-, since O is more electronegative than Br, therefore, –ve charge stays on the O atom. Therefore, in BrO_3^-, there are two Br=O bonds and one Br—O⁻ bond. Now, according to VSEPR theory, double bonds do not contribute any electrons while single bonds contribute one electrons towards the total number of electrons in the valence shell of the central atom. However, both double and single bonds contribute one bond pair. Thus, total number of electrons is the valence shell of the central Br atom = 7 + 2 × 0 + 1 × 1 = 8

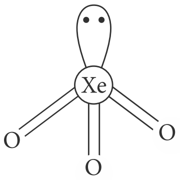
$\therefore$ No. of electrons pairs around Br atom $= \frac{8}{2} = 4$

But total number of bond pairs

$= 2 \times 1\,(Br{=}O) + 1 \times (Br - O^-) = 3$

Thus, lone pairs = 4 – 3 = 1

Thus, BrO_3^- has 3 bond pairs and one lone pair. Therefore, according to VSEPR theory, it should be pyramidal.



Now a noble gas compound having 8 electrons in the valence shell of the central atom is XeO_3.

(ii) Partial hydrolysis of XeF_6 gives $XeOF_4$ and XeO_2F_2

$$\overset{+6\,-1}{XeF_6} + \overset{+1-2}{H_2O} \longrightarrow \overset{+6\,-2\,-1}{XeOF_4} + \overset{+1-1}{2HF}$$

$$\overset{+6\,-1}{XeF_6} + \overset{+1\;\,-2}{2H_2O} \longrightarrow \overset{+6\,-2\,-1}{XeO_2F_2} + \overset{+1-1}{4HF}$$

On the other hand, complete hydrolysis XeF_6 gives XeO_3.

$$\overset{+6\,-1}{XeF_6} + \overset{+1\;\,-2}{3H_2O} \longrightarrow \overset{+6\,-2}{XeO_3} + \overset{+1-1}{6HF}$$

As the oxidation state of all elements in the reactants and products of hydrolysis remains the same. Therefore, these are not the redox reactions.

(iii) $6NaOH + 3Cl_2 \longrightarrow 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$

Yes, this reaction is disproportionation reaction as chlorine from zero oxidation state changes to −1 and +5, oxidation states.

26. **(i)** In blast furnace, reduction of iron oxides takes place in different temperature ranges. The lower part of the blast furnace has high temperature of the order 2200 K (called combustion zone) and the top of the furnace has low temperature of the order 500-800 K (called reduction zone). The reduction occurring in the lower temperature range (upper part) is by carbon and in the higher temperature range (lower part) is by carbon monoxide.

At lower temperature range (500-800 K) in upper part of furnace the reactions occuring are :

$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$

$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$

$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$

At higher temperature range (900-1500 K) in lower part of furnace the reactions occuring are :

$C + CO_2 \longrightarrow 2CO$

$FeO + CO \longrightarrow Fe + CO_2$

In the middle portion (at about 1270 K), limestone decomposes to give lime (CaO) and CO_2. Lime acts as a flux and combines with silicate impurity to form slag.

$CaCO_3 \longrightarrow CaO + CO_2$

$$\underset{\text{Lime}}{CaO} + \underset{\text{Impurity}}{SiO_2} \longrightarrow \underset{\text{Calcium silicate (Slag)}}{CaSiO_3}$$

Slag is in the molten state and separates out from iron.

At the combustion zone, the reaction taking place are :

$FeO + C \longrightarrow Fe + CO$

(ii) **(a)** Zinc blende ore (ZnS) is roasted in the presence of excess air at about 1200 K to convert it to zinc oxide.

$$\underset{\text{Zinc blende}}{2ZnS} + 3O_2 \xrightarrow{\Delta} \underset{\text{Zinc oxide}}{2ZnO} + 2SO_2$$

(b) Zinc oxide is reduced to zinc by heating with crushed coke at 1673 K.

$$ZnO + C \xrightarrow{1673\ K} Zn + CO$$

(c) The impure zinc is refined by electrorefining method. In this method, the impure zinc is made anode and a plate of pure zinc is made cathode in an electrolytic bath containing zinc sulphate and a small amount of dilute H_2SO_4. On passing current, the following reactions occur:

At anode : $Zn \longrightarrow Zn^{2+} + 2e^-$

At cathode : $Zn^{2+} + 2e^- \longrightarrow Zn$

The zinc gets deposited on cathode and is collected.

OR

(i) Zinc being above iron in the electrochemical series, the reduction will be faster where zinc scraps are used. But zinc is costlier than iron so using iron scraps will be advisable and advantageous.

(ii) The standard free energies ($\Delta_f G°$) of formation of most of the sulphide are greater than those of CS_2 and H_2S (CS_2 is in fact, an endothermic compound). Therefore, neither carbon nor hydrogen can reduce metal sulphides to metal. In contrast, the standard free energies of formation of oxides are much lower than that of SO_2 and hence, oxidation of metal sulphides to metal oxides is thermodynamically favorable. Therefore, it is the common practice to roast sulphide ore to the oxide before reduction.

(iii) The chief ore of silver is argentite or silver glance (Ag_2S).

The extraction of silver from argentite : Argentite ore is treated with dilute solution of NaCN in presence of oxygen to form complex.

$$2Ag_2S + 8CN^- + O_2 + 2H_2O \longrightarrow 4[Ag(CN)_2]^- + 2S + 4OH^-$$

Zn act as a reducing agent and displaces silver by fusion with borax or by electrolysis.

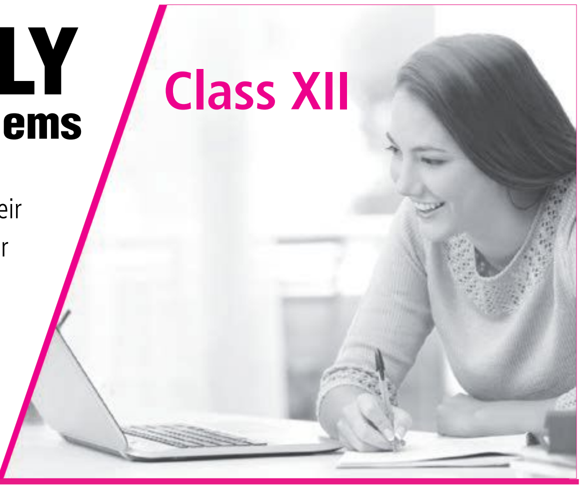
$2[Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Ag$

The crude Ag metal thus obtained is refined by fusion with borax or by electrolysis.

◆◆

MPP-4 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.

The *p*-Block Elements (Group 15 to 18)

Total Marks : 120 **Time Taken : 60 Min.**

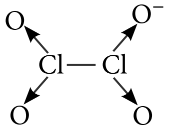
NEET / AIIMS

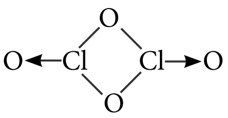
Only One Option Correct Type

1. It is suggested that ammonia bottles should be opened after cooling in ice for sometime. This is because
(a) it brings tears to eyes
(b) it has high vapour pressure
(c) it is corrosive liquid
(d) it is mild explosive.

2. A boy accidently splashes a few drops of conc. H_2SO_4 on his cotton shirt and splashed part blackens and holes appear. This is because, the sulphuric acid
(a) heats up the cotton so that it burns
(b) dehydrates the cotton
(c) causes the cotton to react with oxygen in air
(d) removes the elements of water from cotton.

3. The structure of Cl_2O_4 is

(a) 

(b) 

(c) $Cl^+ClO_4^-$ (d) $ClO^+ ClO_3^-$

4. The reaction between NH_2^- and N_2O gives
(a) NO_2 (b) N_2O_5
(c) NH_2NH_2 (d) N_3^-

5. In solid state, the colour of oxygen has been observed as pale blue. This pale blue colour of oxygen is due to electronic transition from
(a) the triplet ground state to the excited singlet state
(b) the triplet ground state to antibonding $\sigma 2p_z$ molecular orbital
(c) the antibonding π-molecular orbital to the bonding $\sigma 2p_z$ molecular orbital
(d) the singlet ground state to the excited triplet state.

6. A solution of ammonia in water contains
(a) H^+ ions
(b) OH^- ions
(c) NH_4^+ ions
(d) OH^- ions, NH_4^+ ions and NH_4OH molecules.

7. In the reaction, $H_2SO_4 + P_2O_5 \xrightarrow{\Delta} (X) + SO_3$, the product (X) is
(a) PH_3 (b) H_3PO_4
(c) HPO_3 (d) $N_4P_2O_7$

8. The following acids are arranged in the order of decreasing acid strength. The correct order is ClOH(I), BrOH(II), IOH(III)
(a) II > I > III (b) III > II > I
(c) I > II > III (d) I > III > II

9. Which of the following statements are correct?
(i) Carbon monoxide is neutral whereas SO_3 is acidic.
(ii) Potassium oxide is basic whereas nitrous oxide is acidic.
(iii) Aluminium and zinc oxides are amphoteric.
(iv) Sulphur trioxide is acidic whereas phosphorus pentoxide is basic.

(a) Only (ii) and (iii)
(b) Only (i) and (iv)
(c) Only (i) and (iii)
(d) None of these

10. What is the reason for not storing XeF_6 in a glass or a quartz vessel?
(a) It reacts with SiO_2 and forms highly explosive XeO_2F_2.
(b) It reacts with SiO_2 and forms highly explosive XeO_3.
(c) It reacts with SiO_2 and forms highly explosive XeO_2.
(d) It reacts with SiO_2 and forms highly explosive XeO_6^{4-}.

11. The possible reaction is
(a) $K[BrICl] \xrightarrow{\Delta} KCl + IBr$
(b) $K[BrICl] \xrightarrow{\Delta} KBr + ICl$
(c) $K[BrICl] \xrightarrow{\Delta} KI + BrCl$
(d) All of the above.

12. PH_3 and NH_3 on reacting separately with bleaching powder produce respectively
(a) P and N_2
(b) PCl_3 and NCl_3
(c) PCl_3 and N_2
(d) PCl_5 and NCl_3

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 :** $SeCl_4$ does not possess tetrahedral structure.
Reason : Se in $SeCl_4$ has two lone pairs.

14. **Assertion :** NO_3^- is planar while NH_3 is pyramidal.
Reason : N in NO_3^- is sp^2 hybridised but in NH_3 it is sp^3 hybridised.

15. **Assertion :** Salts of ClO_3^- and ClO_4^- are well known but those of FO_3^- and FO_4^- are not known.
Reason : F is more electronegative than O while Cl is less electronegative than O.

JEE MAIN / JEE ADVANCED

Only One Option Correct Type

16. The temperature at which α and β forms of sulphur are at equilibrium is known as
(a) critical temperature
(b) transition temperature
(c) Boyle's temperature
(d) inversion temperature.

17. What is the product formed when phosphorus acid is allowed to react with sufficient quantity of KOH?
(a) K_3PO_3
(b) KH_2PO_3
(c) K_2HPO_3
(d) $KHPO_3$

18. Which of the following reactions is not feasible spontaneously?
(a) $H_2O + F_2 \rightarrow HF + HOF$
(b) $H_2O + Cl_2 \rightarrow HCl + HOCl$
(c) $H_2O + Br_2 \rightarrow 2HBr + [O]$
(d) $H_2O + I_2 \rightarrow 2HI + [O]$

19. Of the interhalogen AX_3 compounds; ClF_3 is most reactive but BrF_3 has higher conductance in liquid state because
(a) BrF_3 has higher molecular mass
(b) ClF_3 is more volatile
(c) BrF_3 dissociates into BrF_2^+ and BrF_4^- most easily
(d) electrical conductance does not depend on concentration.

More than One Options Correct Type

20. The nitrogen oxides that contain N—N bonds are
(a) N_2O
(b) N_2O_3
(c) N_2O_4
(d) N_2O_5

21. The final product formed from the electrolysis of 50% H_2SO_4 with high current density, has

Solution Senders of Chemistry Musing

Set - 48

- Ravinder Kashapogu, Telangana
- Ashwin Thakur, Kerala
- Kartik Taneja, Punjab

(a) S—O—O—S linkage
(b) O—O linkage
(c) S—S linkage
(d) S—O—S linkage.

22. Which among the following statements are correct?
(a) The correct order of occurrence (% by weight) in the air is Ar > Ne > Kr.
(b) In the separation of noble gases by Dewar's method, the principle used is fractional distillation.
(c) The boiling point order of noble gases is He < Ar < Kr < Xe.
(d) Xenon forms fluorides, oxides and oxyfluorides in excited states.

23. Which of the following statements are correct?
(a) Chlorine dioxide (ClO_2) is powerful oxidising agent but its bleaching action is lower than Cl_2.
(b) ClO_2 in alkaline solution undergoes disproportionation.
(c) ClO_2 is diamagnetic in nature.
(d) ClO_2 is a yellow gas but deep red liquid.

Integer Answer Type

24. The number of orbitals involved in the hybridisation of sulphur in SCl_2 are

25. The basicity of pyrophosphoric acid is

26. Number of P—O—P bonds in P_4O_{10} is

Comprehension Type

Bleaching powder and bleach solution are produced on a large scale and used in several house-hold products. The effectiveness of bleach solution is often measured by iodometry.

27. The anhydride of oxoacid which is constituent of bleaching powder is
(a) Cl_2O (b) Cl_2O_7 (c) ClO_2 (d) Cl_2O_6

28. 40 mL of house-hold bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.40 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the house-hold bleach solution is
(a) 0.48 M (b) 0.96 M (c) 0.24 M (d) 0.024 M

Matrix Match Type

29. Match the Column I with Column II and mark the appropriate option.

Column I	Column II
(A) HOCl	(P) Monobasic acid
(B) HOClO	(Q) Most acidic
(C) $HOClO_2$	(R) Thermal stability is maximum
(D) $HOClO_3$	(S) Most oxidising
	(T) +ve oxidation state

	A	B	C	D
(a)	P, S, T	R, T	R, T	Q, S
(b)	P, S, T	P, T	P, T	P, Q, R, T
(c)	Q, S, T	P, T	Q, R	P, S, T
(d)	P, Q	S, T	R	P, S, T

30. Match the Column I with Column II and mark the appropriate option.

Column I (Oxoacids)	Column II (Materials for preparation)
(A) $(HPO_3)_n$	(i) $PCl_3 + H_3PO_3$
(B) H_3PO_4	(ii) Red P_4 + alkali
(C) $H_4P_2O_6$	(iii) $P_4O_{10} + H_2O$
(D) $H_4P_2O_5$	(iv) Phosphorus acid + Br_2, heat in a sealed tube

(a) (A)-(iii); (B)-(iv); (C)-(ii); (D)-(i)
(b) (A)-(iv); (B)-(iii); (C)-(ii); (D)-(i)
(c) (A)-(ii); (B)-(i); (C)-(iv); (D)-(iii)
(d) (A)-(i); (B)-(iii); (C)-(iv); (D)-(ii)

◆ ◆

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.

CHEMISTRY MUSING

PROBLEM SET 49

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER 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.

JEE MAIN/NEET

1. A *bcc* lattice is made up of hollow spheres of X. Spheres of solids 'Y' are present in hollow spheres of X. The radius of 'Y' is half of the radius of 'X'. What will be the ratio of total volume of spheres of 'X' unoccupied by 'Y' in a unit cell and volume of the unit cell?

(a) $\frac{7\pi\sqrt{3}}{64}$ (b) $\frac{7\pi\sqrt{3}}{8}$

(c) $\frac{5\pi\sqrt{3}}{64}$ (d) $\frac{\pi\sqrt{3}}{64}$

2. A molecule having formula PQ_2H_8 has the following structural features (H is hydrogen atom):

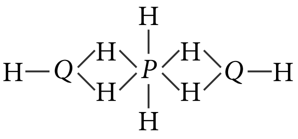
I. P and Q both belong to period 2 of periodic table .

II. P and Q have two and three valence electrons respectively.

III. There are four $(2c - 2e^-)$ bonds and four $(3c - 2e^-)$ bonds in the molecule.

IV. In P and Q both form atleast one $(2c - 2e^-)$ bond.

Based on above structural information which one of the following structures is most appropriate for PQ_2H_8?

(a)


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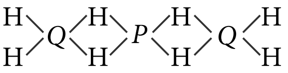
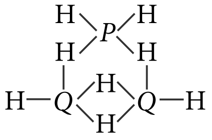
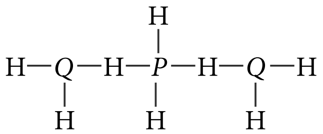
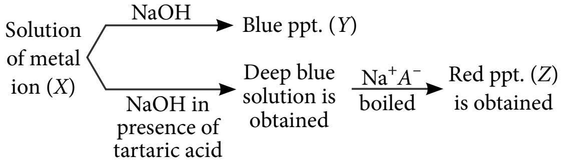


(c)


(d)


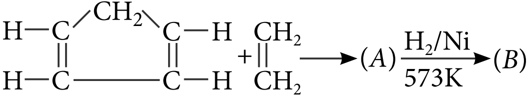
3.


The cation, X and anion, A are respectively

(a) NH_4^+, $CH_3CO_2^-$ (b) HCO_2^-, Cu^{2+}

(c) Pb^{2+}, $C_2O_4^{2-}$ (d) Cu^{2+}, HCO_2^-

4. Complete the following reaction :



Name of compound B is

(a) bicyclo(2,2,1)–2–heptene

(b) bicyclo(2,2,1)–heptane

(c) bicyclo(2,2,0) – heptane

(d) cycloheptane.

5. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25 °C) is titrated with $\frac{2}{15}$ M HCl in water at 25 °C. The concentration of H^+ ions at equivalence point is

(a) 3.7×10^{-13} M (b) 3.2×10^{-7} M

(c) 3.2×10^{-2} M (d) 2.7×10^{-2}M

JEE ADVANCED

6. 22.44 kJ energy is required to convert 8 g of gaseous atom of metal M to $M^+_{(g)}$. If $I.E._1$ of metal M = 374 kJ/mole. Select the correct option for the above metal M.

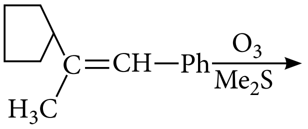
(a) 0.6 mole gaseous ion (M^+) are formed.

(b) Same energy can convert all $M^+_{(g)}$ to $M^{2+}_{(g)}$.

(c) Atomic mass of metal = 153.33.

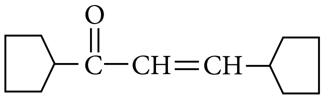
(d) 3.613×10^{22} atoms of M are converted to $M^+_{(g)}$.

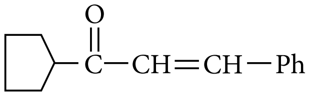
COMPREHENSION

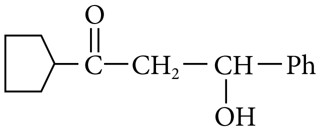


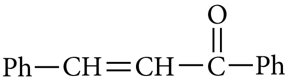
$$A + B \xrightarrow{Ca(OH)_2 + I_2} C + D \xrightarrow{\Delta} E + CaCO_3$$

7. $A + B \xrightarrow[\Delta]{NaOH}$ Product. The product formed is

(a) 

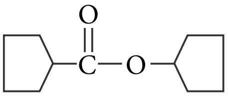
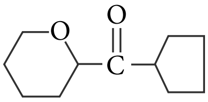
(b) 

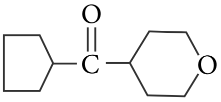
(c) 

(d) 

$Ph{-}CH{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Ph$

8. $E \xrightarrow{CF_3CO_3H}$ Product. The product formed is

(a)  (b) 

(c)  (d) None of these.

INTEGER VALUE

9. The freezing point of an aqueous solution of KCN, containing 0.1892 mole/kg water, was – 0.704 °C. On adding 0.095 mole of $Hg(CN)_2$, the freezing point of the solution was – 0.53 °C. Assuming that the complex is formed according to the equation:

$$Hg(CN)_2 + xCN^- \rightarrow [Hg(CN)_{x+2}]^{x-}$$

and also $Hg(CN)_2$ is the limiting reactant. The value of x is

10. Accelerating potential needed to produce an electron beam with wavelength 8.7 pm is $x \times 10^4$ V. The value of x is

◆◆

JEE Advanced

PRACTICE PROBLEMS

SECTION 1 (Maximum Marks : 18)

This section contains 6 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct. For each question you will be awarded 3 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.

1. A sample of argon gas at 1 atm pressure and 27 °C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. ($C_{v,\,m}$ for argon is 12.48 J K^{-1} mole^{-1})

$$\left(\text{Given} : \left(\frac{1}{2}\right)^{0.66} = 0.632\right)$$

(a) –4.52 J (b) –14.52 J
(c) –114.78 J (d) –228.52 J

2. How much heat is required to change 10 g ice at 0° C to steam at 100° C? Heat of fusion and heat of vaporisation for water are 80 cal/g and 540 cal/g respectively. (Specific heat of water is 1 cal/g/K).

(a) 2 cal (b) 200 cal
(c) 5028 cal (d) 7200 cal

3. 5 mol of ideal gas at 27°C expands isothermally and reversibly from volume of 6 L to 60 L. The work done (in kJ) is

(a) –14.7 (b) –28.72
(c) –36.72 (d) –56.72

4. The value of ΔH_f° of U_3O_8 is –853.5 kJ mol^{-1}.

Also, ΔH° for the reaction :

$3UO_2 + O_2 \rightarrow U_3O_8$, is –76.00 kJ.

The value of ΔH_f° of UO_2 is approximately

(a) –259.17 kJ (b) –310.17 kJ
(c) +259.17 kJ (d) 930.51 kJ

5. The standard molar enthalpies of formation of cyclohexane$_{(l)}$ and benzene$_{(l)}$ at 25°C are –156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene$_{(l)}$ at 25°C is –119 kJ/mol. Find the magnitude of resonance energy in benzene.

(a) 152 kJ mol^{-1} (b) 102 kJ mol^{-1}
(c) 168 kJ mol^{-1} (d) 86 kJ mol^{-1}

6. Consider these two statements :

(I) The reversible work done by 2 moles of an ideal gas, isothermally at 300 K, as it expands from 10 atm to 1 atm pressure, is roughly –2.764 kcal.

(II) 2 moles of a gas expand against a constant pressure of 1 atm, the change in the volume being 82.12 mL. The work done by the gas is roughly –3 cal.

Choose the correct options.

(a) (I) and (II) are correct.
(b) (I) and (II) are incorrect.
(c) (I) is incorrect and (II) is correct.
(d) (I) is correct and (II) is incorrect.

SECTION 2 (Maximum Marks : 08)

This section contains 2 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which one or more than one answer is correct. For each question you will be awarded 4 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marking in this section.

7. The standard state Gibbs free energies of formation of $C_{(graphite)}$ and $C_{(diamond)}$ at T = 298 K are

$\Delta_f G^\circ[C_{(graphite)}] = 0$ kJ mol^{-1}

$\Delta_f G^\circ\ [C_{(diamond)}] = 2.9$ kJ mol^{-1}.

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite $[C_{(graphite)}]$

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to diamond[$C_{(diamond)}$] reduces its volume by 2×10^{-6} m^3 mol^{-1}. If $C_{(graphite)}$ is converted to $C_{(diamond)}$ isothermally at $T = 298$ K, the pressure at which $C_{(graphite)}$ is in equilibrium with $C_{(diamond)}$, is
(Useful information : 1 J = 1 kg m^2 s^{-2} ;
1 Pa = 1 kg m^{-1} s^{-2}; 1 bar = 10^5 Pa)

(a) 14501 bar (b) 29001 bar
(c) 1450 bar (d) 58001 bar

8. What is true about the expression,
$6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(l)} + x$ kJ?
(a) ΔH_f of C_6H_6 is $-x$ kJ mol^{-1}.
(b) The equation is arithmetically true.
(c) The equation is chemically true.
(d) Heat of atomization of C_6H_6 is $+ x$ kJ mol^{-1}.

SECTION 3 (Maximum Marks : 24)

This section contains 6 integer type questions. Answers are to be given in between 0 to 9 in the form of nearest integer. Each question carries 4 marks if you darken the correct answer and no negative mark will be awarded for an incorrectly bubbled answer.

9. The ionization energy of rubidium is (90 + P) kcal/mole using the following diagram. (Energies in kcal/mole). Find 'P'.

$$\begin{tikzcd}
Rb_{(s)} \arrow[dd, "20.5"'] & +\frac{1}{2}Cl_{2(g)} \arrow[r, "-102.9"] \arrow[d, "27"] & RbCl_{(s)} \\
 & Cl_{(g)} \arrow[r, "-79.5"] & Cl^-_{(g)} \arrow[u, "-166"'] \\
Rb_{(g)} \arrow[rr, "I.E."] & & +\ Rb^+_{(g)}
\end{tikzcd}$$

10. The amount of ice that will remain when 52 g of ice is added to 100 g of water at 40°C is ______ g at the stage of thermal equilibrium at 0°C. (Given : Specific heat of water is 1 cal/g/K and latent heat of fusion is 80 cal/g.)

11. One mole of monoatomic ideal gas at $P = 2$ bar and $T = 273$ K is compressed to 4 bar pressure following a reversible path, obeying P/V = constant. Assume $C_v = 12.5$ J mol^{-1} K^{-1}. The value of $\frac{\Delta U}{W}$ for this process is minus________.

12. Out of the following properties how many are path functions?
Heat enthalpy, Internal energy, Temperature, Work, Heat, Specific heat

13. 10 mL of dissolution of a strong acid (HA) on mixing with 10 mL of strong alkali (BOH) at the same temperature shows a temperature rise of 4°C. If 50 mL of same acid is mixed with 50 mL of same alkali; the temperature rise will be ________ °C. Assume all the heat produced is used up in increasing temperature of mixture only.

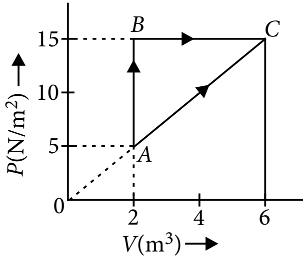
14. The enthalpy change involved in the oxidation of glucose is -2880 kJ mol^{-1}. 25% of this energy is available for muscular work. If 80 kJ of muscular work is needed to walk one km, what is the maximum distance that a person will walk after eating 120 g glucose.

SECTION 4 (Maximum Marks : 06)

This section contains 1 paragraph. Based upon paragraph, 2 multiple choice questions have to be answered. For each question you will be awarded 3 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.

PARAGRAPH

The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas.



15. Calculate the path along which work done is least.
(a) AB (b) BC (c) AC (d) All are equal

16. Amount of heat supplied to the gas to go from A to B, if internal energy change of gas is 10 J.
(a) 5 J (b) 10 J (c) 15 J (d) 20 J

SECTION 5 (Maximum Marks : 16)

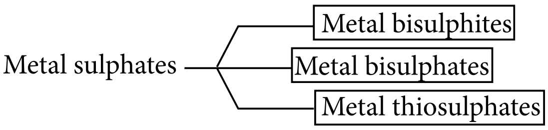
This section contains 2 questions. Each question contains statements given in 2 columns. Statements in the first column have to be matched with statements in the second column. For each question in this section, you will be awarded 8 marks if you darken all the bubbles corresponding only to the correct answer and 2 marks for each row. No negative mark will be awarded for an incorrectly bubbled answer.

Contd. on Page No. 82

CONCEPT BOOSTER

> Hello Champs!! First of all heartiest thanks for appreciating my last article through emails and messages. I convey my sincere gratitude for the same. This article is in the continuation of the last article and the motive of this article is to save you from the phobia of Inorganic Chemistry. I have tried to make the things simple so that INORGANIC CHEMISTRY doesn't appear to be a gobbledygook for you all. Hope you will like and enjoy it.
>
> *Arunava Sarkar

HEATING EFFECTS



There are some different trends in this case. Take the first logic,

$$\underset{\text{(Metal sulphate)}}{MSO_4} \xrightarrow{< 1073\text{ K}} MO + SO_3\uparrow$$

$$\underset{\text{(Metal sulphate)}}{MSO_4} \xrightarrow{> 1073\text{ K}} MO + SO_2\uparrow + \frac{1}{2}O_2\uparrow$$

i.e. at temperature greater than 1073 K, SO_3 decomposes into SO_2 and O_2.

Now, which sulphate decomposes on heating and which is not, there is a good logic behind this.

Logic : Salts where more polarisation takes place, become more covalent and thermally unstable. So, they decompose on heating. On the other hand, salts where less polarisation takes place, they become more ionic and thermally more stable. They do not decompose easily. That's why Li_2SO_4 decomposes easily on heating but Na_2SO_4, K_2SO_4, Rb_2SO_4, Cs_2SO_4, etc. do not decompose easily on heating.

$$Li_2SO_4 \xrightarrow{\Delta} Li_2O + SO_3$$

Thermal stability order is :

$$\underset{\text{Increasing thermal stability}}{\underrightarrow{Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Pb_2SO_4 < Cs_2SO_4}}$$

In the similar way,

$$\underset{\text{Thermal stability increases}}{\underrightarrow{BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4 < BaSO_4}}$$

Now, let us take the case of hydrated salts :

1. Blue vitriol :

$$\begin{tikzcd}
\underset{\text{Blue Vitriol}}{CuSO_4\cdot5H_2O} \arrow[r, "100°C", "-4H_2O"'] & \underset{\text{Bluish white colour}}{CuSO_4\cdot H_2O} \arrow[d, "220°C", "-H_2O"'] \\
\underset{\text{(Black)}}{CuO + SO_3} & \underset{\text{White}}{CuSO_4} \arrow[l, "750°C"'] \arrow[dl, "> 800°C"] \\
\underset{(SO_3\text{ even decomposes})}{CuO + SO_2 + \frac{1}{2}O_2} &
\end{tikzcd}$$

2. White vitriol :

$$\begin{tikzcd}
\underset{\text{White Vitriol}}{ZnSO_4\cdot7H_2O} \arrow[r, "70°C", "-H_2O"'] & ZnSO_4\cdot6H_2O \arrow[d, "> 70°C", "< 200°C \; -5H_2O"'] \\
ZnSO_4 \arrow[d, "> 800°C"] & ZnSO_4\cdot H_2O \arrow[l, "> 200°C"'] \\
ZnO + SO_2 + \frac{1}{2}O_2 &
\end{tikzcd}$$

3. Epsom salt :

It works in the similar manner as $ZnSO_4\cdot7H_2O$ does.

$$\begin{tikzcd}
\underset{\text{Epsom salt}}{MgSO_4\cdot7H_2O} \arrow[r, "150°C", "-6H_2O"'] & MgSO_4\cdot H_2O \arrow[d, "200°C"] \\
MgO + SO_2 + \frac{1}{2}O_2 & \underset{\text{(anhydrous)}}{MgSO_4} \arrow[l, "1000°C"']
\end{tikzcd}$$

---

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4. Green vitriol :

$$\underset{\text{Green vitriol}}{FeSO_4{\cdot}7H_2O} \xrightarrow[-7H_2O]{300^\circ C} FeSO_4$$

(important: all crystal water molecules gone)

($FeSO_4{\cdot}7H_2O$ behaves unconventionally in every aspect.)

$$2FeSO_4 \xrightarrow{\Delta} \underbrace{Fe_2O_3 + SO_2 + SO_3}$$

You must remember this as a very important exceptional case.

5. Gypsum :

$$\underset{\text{Gypsum}}{CaSO_4{\cdot}2H_2O} \xrightarrow{120^\circ C} \underset{\text{Plaster of Paris}}{CaSO_4{\cdot}\tfrac{1}{2}H_2O}$$

$$\downarrow \Delta$$

$$\underset{\text{Dead burnt}}{\underbrace{CaSO_4}} + \tfrac{1}{2}H_2O$$

Important : Convert

Plaster of Paris ⟶ Gypsum

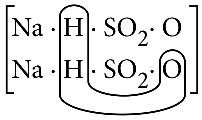
$$\underset{\text{Plaster of Paris}}{CaSO_4{\cdot}\tfrac{1}{2}H_2O} \xrightarrow{+1\frac{1}{2}H_2O} \underset{\text{Gypsum}}{CaSO_4{\cdot}2H_2O}$$

Important and unconventional sulphate, thiosulphate, bisulphite and bisulphate salts :

1. $\overset{+3}{Fe_2}(SO_4)_3 \xrightarrow{\Delta} \overset{+3}{Fe_2}O_3 + 3SO_3$ (important)

Shortcut : Heating (strongly) in general which causes simple decomposition and doesn't bring oxidation number down.

2. $2NaHSO_3 \xrightarrow[-H_2O]{\Delta} Na_2\overset{+4}{S_2}O_5 \xrightarrow{\Delta} Na_2\overset{+4}{S}O_3 + SO_2$



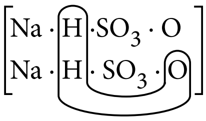
Discussed shortcut above

Δ, disproportionation

$$Na_2S + Na_2SO_4$$

$$(4Na_2\overset{+4}{S}O_3 \xrightarrow{\Delta} Na_2\overset{-2}{S} + 3Na_2\overset{+6}{S}O_4)$$

3. $2NaHSO_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{unstable}}{[Na_2S_2O_7]} \xrightarrow{\Delta} Na_2SO_4 + SO_3$



4. $Na_2S_2O_3{\cdot}5H_2O \xrightarrow{220^\circ C} Na_2S_2O_3 + 5H_2O$

(Thiosulphate or Hypo)

$$4Na_2S_2O_3 \xrightarrow{\Delta} 3Na_2SO_4 + Na_2S_5$$

HEATING EFFECT ON HALIDE SALTS

Chlorine at comparatively lower +ve oxidation state

$$\left[\begin{array}{l} 3\overset{+1}{Cl}O^- \xrightarrow{\Delta} 2Cl^- + \overset{+5}{Cl}O_3^- \\ \overset{+3}{Cl}O_2^- \xrightarrow{\Delta} Cl^- + 2\overset{+5}{Cl}O_3^- \end{array}\right]$$

Chlorine not at higher +ve oxidation state *i.e.* +7. It is just below that.

$$4\overset{+5}{Cl}O_3^- \xrightarrow{\Delta} Cl^- + 3\overset{+7}{Cl}O_4^-$$

Chlorine at comparatively higher oxidation state.

Chlorine at the highest +ve oxidation state.

Now, take the following shortcut :

Short-cut : Heating metal halides (specially metal chlorides) bring the metal at lower oxidation state either with the halide or the pure metal. Take the following examples :

- ❍ $2\overset{+3}{Fe}Cl_3 \xrightarrow{\Delta} 2\overset{+2}{Fe}Cl_2 + Cl_2$ (lower state)
- ❍ $\overset{+3}{Au}Cl_3 \xrightarrow{\Delta} \overset{+1}{Au}Cl + Cl_2$ (lower state) [Au maintaining only +3 and +1 states in comopunds.]
- ❍ $PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$ (lower state) [Due to inert pair effect Pb^{2+} is more stable than +4.]
- ❍ $PbBr_4 \xrightarrow{\Delta} PbBr_2 + Br_2$

  [**Note :** PbI_4 doesn't exist]
- ❍ $\underset{\text{(solid)}}{NH_4Cl} \xrightarrow{\Delta} NH_3 + HCl$
- ❍ $\overset{+1}{Hg_2}Cl_2 \longrightarrow \overset{+2}{Hg}Cl_2 + \overset{0}{Hg}$ $\left[\dfrac{+2+0}{2} = +1\right]$

  Look! It has increased here. Because there is a Hg with 0 oxidation state.

  Again shortcut works.

Some more cases :

- ❍ **Heating of bleaching powder :**

$$Ca(OCl)Cl \xrightarrow[CoCl_2\,\text{catalyst}]{\text{strong heating}} CaCl_2 + \tfrac{1}{2}O_2$$

- ❍ **Heating of potassium chlorate ($KClO_3$) :**

$$2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$$

HEATING EFFECT ON HYDRATED CHLORIDE SALTS

Metal oxides and HCl become the end products with little bit exception in some cases. (like hydrated cobalt chloride).

- $$\begin{array}{l} MgCl_2\cdot 6H_2O \longrightarrow Mg(OH)Cl + HCl + 5H_2O \\ Mg(OH)Cl \longrightarrow MgO + HCl \\ \hline MgCl_2\cdot 6H_2O \longrightarrow MgO + 2HCl + 5H_2O \end{array}$$
- $2AlCl_3\cdot 6H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl + 9H_2O$
- $2FeCl_3\cdot 6H_2O \xrightarrow{\Delta} Fe_2O_3 + 6HCl + 9H_2O$
- $$\begin{tikzcd} \underset{\text{Pink}}{CoCl_2\cdot 6H_2O} \arrow[r, "50°C\text{-}55°C", "-2H_2O"'] & \underset{\text{Pale pink}}{CoCl_2\cdot 4H_2O} \arrow[d, "-2H_2O"', "60°C"] \\ \underset{\text{Blue}}{CoCl_2} & \underset{\text{Red violet}}{CoCl_2\cdot 2H_2O} \arrow[l, "140°C\text{-}150°C"', "-2H_2O"] \end{tikzcd}$$

HEATING EFFECT ON OXIDE SALTS

Two things may happen due to heating of oxide salts :

1. Chemical change
2. Physical change (specially colour change).

Most importantly, shortcut for Hg and Ag also work here. Take the following examples :

1. $\overset{+1}{2Ag_2O} \xrightarrow[300°C]{\Delta} \overset{0}{4Ag} + O_2$

   [**Note :** Heating of oxides always bring down the oxidation number of metal]

2. $\overset{+6}{2CrO_3} \longrightarrow \overset{+3}{Cr_2O_3} + \frac{3}{2}O_2$
3. $\overset{+6}{2CrO_5} \longrightarrow \overset{+3}{Cr_2O_3} + \frac{7}{2}O_2$
4. $\overset{+4}{PbO_2} \longrightarrow \overset{+2}{PbO} + \frac{1}{2}O_2$
5. $\overset{+4}{3MnO_2} \xrightarrow{900°C\text{-}1000°C} \overset{+8/3}{Mn_3O_4} + O_2$
6. $\underset{\text{Red lead}}{2Pb_3O_4} \underset{350°C}{\overset{500°C}{\rightleftarrows}} \underset{\text{litharge}}{6PbO} + O_2$
7. $\underset{\text{White}}{ZnO} \underset{\text{cold}}{\overset{\text{hot}}{\rightleftarrows}} \underset{\text{Yellow}}{ZnO}$
8. $\underset{\underset{\text{(Massicot)}}{\text{yellow}}}{PbO} \underset{\text{cold}}{\overset{\text{hot}}{\rightleftarrows}} \underset{\underset{\text{(Litharge)}}{\text{red}}}{PbO}$
9. $\underset{\text{(Yellow)}}{HgO} \xrightarrow{\Delta} \underset{\text{(Red)}}{HgO} \xrightarrow{> 400°C} Hg + \frac{1}{2}O_2$

[**Note :** $I_2O_5 \xrightarrow{\Delta} I_2 + \frac{5}{2}O_2$]

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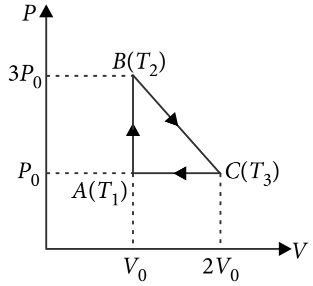
Contd. from Page No. 79

JEE Advanced

PRACTICE PROBLEMS

17. One mole of an ideal monoatomic gas is taken a round cyclic process *ABCA* as shown in figure.



	Column I (Thermodynamics properties)		Column II
(A)	The work done by the gas	(p)	$\frac{3P_0V_0}{R}$
(B)	The heat rejected by the gas in the path *CA*	(q)	$+3P_0V_0$
(C)	The heat absorbed by the gas in the path *AB*	(r)	$-\frac{5}{2}P_0V_0$
(D)	The temperature T_2 is	(s)	$-P_0V_0$

18. Two moles of a perfect gas undergo the following processes :

(i) A reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L).
(ii) A reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L).
(iii) A reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).

	Column I (Thermodynamics properties)		Column II (in Joules)
(A)	Total work	(p)	0
(B)	Total heat changed	(q)	300
(C)	ΔU	(r)	–622.1
(D)	ΔS	(s)	622.1

ANSWER KEY

1. (c) **2.** (d) **3.** (b) **4.** (a) **5.** (a)
6. (d) **7.** (a) **8.** (a, b) **9 .** (5) **10.** (2)
11. (3) **12.** (3) **13.** (4) **14.** (6) **15.** (c)
16. (b) **17.** (A) - (s), (B) - (r), (C) - (q), (D) - (p)
18. (A) - (r), (B) - (s), (C) - (p), (D) - (p)

For detailed solutions to the JEE Advanced Practice Problems visit our website: www.vidyalankar.org

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ADVANCED CHEMISTRY BLOC

(BASIC STRENGTH OF COMMON COMPOUNDS)

Mk C R ay,O id sha

The basicity that we mostly consider in the branch of Organic Chemistry is the Bronsted basicity; the ability to accept a proton. Now come straight to the points.

NITROGEN AND PHOSPHORUS BASES

The effect of substituting hydrogen by alkyl groups on the nitrogen and phosphorus bases is shown in the table :

Base (*B*)	**pK_a (*B*H$^+$)**
NH_3	9.24
CH_3NH_2	10.6
$(CH_3)_2NH$	10.7
$(CH_3)_3N$	9.8

The basicity order is :

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

The tertiary amine is in an anomalous position with respect to the others. We suspect immediately that solvation is the culprit.

Base (*B*)	**pK_a (*B*H$^+$)**
PH_3	−12
n-$C_4H_9PH_2$	0
$(n$-$C_4H_9)_2PH$	4.5
$(n$-$C_4H_9)_3P$	8.4

In gas phase, the basicity order is :

$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

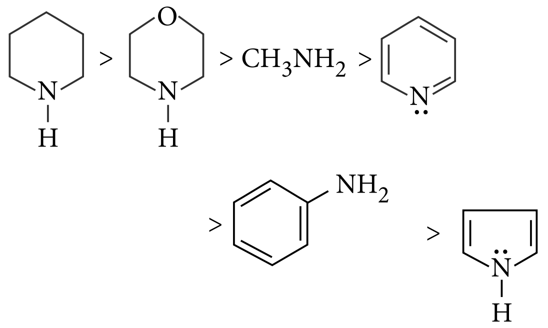
and $(n\text{-}C_4H_9)_3P > (n\text{-}C_4H_9)_2PH > n\text{-}C_4H_9PH_2 > PH_3$

As you can see, the phosphines gave the same order as in gaseous phase that in solution. Moreover, the phosphorus basicities are much more strongly affected than nitrogen basicities on alkyl substitution. (Check the pK_a values)

For some compounds, the gas phase basicity is written as : (least basic first)

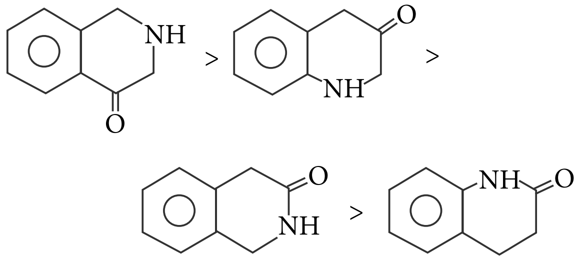
$H_2O < H_2S < CH_3SH < CH_3OH < PH_3 < NH_3 < PhNH_2 < Ph_2NH < CH_3NH_2 < Ph_3N < (CH_3)_2PH < (CH_3)_2NH < (CH_3)_3P < (CH_3)_3N$

Resonance and inductive effect together can explain this. From examination point of view, you must check the following orders :



Pyridine is more basic than aniline. In aniline, the lone pair is in resonance with the ring. Pyrrole is least basic as its lone pair is a part of the aromatic system.

Amides are very little basic. In fact, amides are the weakest of all nitrogenous bases. Now, the following trend is due to —CO— group and Ar-ring.



Both these lower the availability of lone pair on nitrogen, hence lower basicity. In the last compound, both —Ar and —CO— together act on nitrogen lone pair.

Guanidine is the strongest of all nitrogenous bases. The double bonded nitrogen is more basic as its protonated form is stabilised by resonance.

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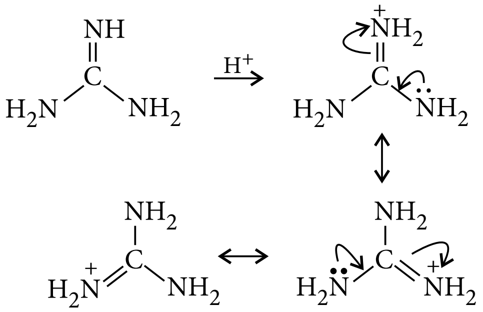
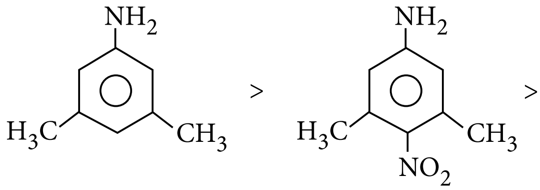
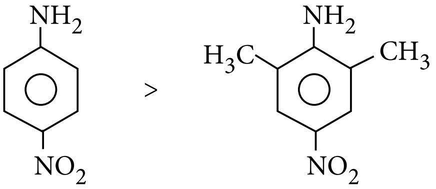


Again,

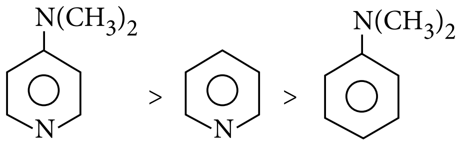




Compound listed in number two position in the above trend is a perfect example where steric inhibition of resonance takes place.

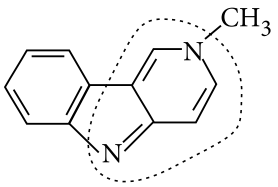
The two $—CH_3$ groups push $—NO_2$ group out of the plane and hence, the $–R$ influence of $—NO_2$ does not operate properly.

Also,

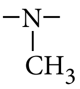


The former two compounds are basic due to ring nitrogen.

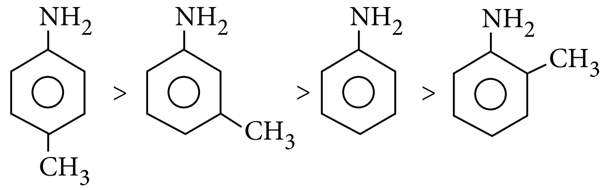
The following compound is most basic at the 'N' atom of the five-membered ring.



This resembles guanidine skeleton

The protonated form is stabilised through resonance by electron donation from  $-\underset{CH_3}{\underset{|}{N}}-$ group.

Another important example is :



The *o*-methyl derivative is least basic due to '*ortho*-effect'.

OXYGEN AND SULPHUR BASES

The following list gives the pK_a values of conjugate acids of some bases in solution.

Base (B)	pK_a (BH^+)
H_2O	–1.74
CH_3OH	–2.05
CH_3CH_2OH	–1.94
CH_3OCH_3	–2.48
CH_3SCH_3	–6.99
CH_3COCH_3	–2.85

In solution phase, dimethyl sulphide is a considerably weaker base than dimethyl ether; while in the gas phase it is slightly stronger. The greater solvation of oxonium ion compared with the sulphonium ion is responsible.

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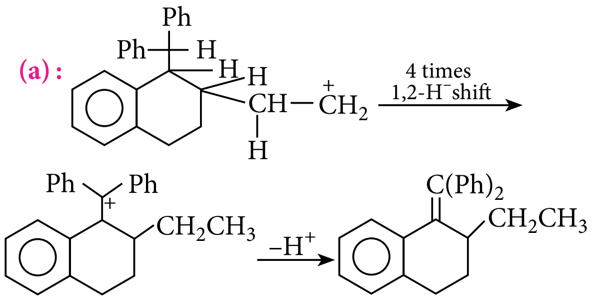
CHEMISTRY MUSING

SOLUTION SET 48

1. (a):



(A)
major

2. (b): 25 cm^3 of undecomposed oxalic acid required
= 32 cm^3 of 0.1 N $KMnO_4$ solution
Thus, 250 cm^3 of undecomposed oxalic acid required
= 320 cm^3 0.1 N $KMnO_4$ solution
= 32 cm^3 1 N $KMnO_4$ solution
≡ 32 cm^3 1 N oxalic acid solution
Oxalic acid used by pyrolusite
= (50 – 32) cm^3 of 1 N solution = 18 cm^3 1 N solution
= 18 cm^3 of 1 N MnO_2 solution

$$\text{Mass of } MnO_2 = \frac{N \times E \times V}{1000} = \frac{1 \times 18 \times 87}{1000 \times 2} = 0.783 \text{ g}$$

$$\text{Percentage of } MnO_2 = \frac{0.783}{1.6} \times 100 = 48.9$$

3. (b): Initial $[Sr^{2+}] = 16 \times 10^{-3}$ M
Final $[Sr^{2+}] = 2.5 \times 10^{-3}$ M
$[Sr^{2+}]$precipitated $= (16 - 2.5) \times 10^{-3} = 13.5 \times 10^{-3}$ M
$[F^-]$ needed for this precipitation $= 2 \times 13.5 \times 10^{-3}$ M
$= 27.0 \times 10^{-3}$ M $\quad (\because\ Sr^{2+} + 2F^- \longrightarrow SrF_2)$
Also, $[Sr^{2+}][F^-]^2 = K_{sp} = 2.8 \times 10^{-9}$

$$\therefore\quad [F^-]^2 = \frac{2.8 \times 10^{-9}}{2.5 \times 10^{-3}}$$

$\therefore\quad [F^-] = 1.058 \times 10^{-3}$ M, *i.e.*, the concentration of F^- which will also appear in solution state.
Thus, $[F^-]$ needed $= [27.0 + 1.058] \times 10^{-3}$ M
$= 28.058 \times 10^{-3}$ M
$\therefore\quad$ NaF needed for 1 L $= 28.058 \times 10^{-3} \times 42$ g

$$\therefore\quad \text{NaF needed for 100 mL} = \frac{28.058 \times 10^{-3} \times 42}{10} \text{ g}$$
$$= 0.1178 \text{ g}$$

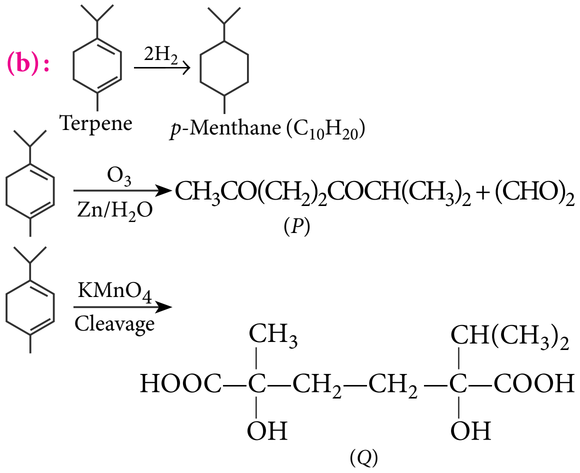
4. (c): $\underset{(Z)}{2B + 3F_2} \longrightarrow \underset{(X)}{2BF_3}$

$\underset{(X)}{8BF_3} + 6LiH \longrightarrow \underset{(Y)}{B_2H_6} + 6LiBF_4$

$B_2H_6 \xrightarrow{\text{Red heat}} 2B + 3H_2$

5. (c)

6. (b):



7. (a): Percentage of backside attack = Percentage of inversion + $\frac{1}{2}$ (Percentage of racemisation)

$$30 + \frac{1}{2}(70) = 65\%$$

70% racemisation and rest 30% inversion gives 65% backside attack.

8. (c): The substrate though is a primary halide but it is excessively branched at the β-position. Such substrate fails miserably in S_N2 reaction even though it is a primary halide. Being a primary halide, it does not react actively in S_N1 mechanism as well. However, it reacts quite fluently by S_N1 mechanism in presence of Ag^+ catalyst.

9. (2): 1 mole of H_2O = 18 g = 18 cm^3
$(\because d_{H_2O} = 1 \text{ g cm}^{-3})$
$= 6.022 \times 10^{23}$ molecules of H_2O
Therefore, volume of 1 molecule of H_2O

$$= \frac{18}{6.022 \times 10^{23}} \text{cm}^3 = 2.989 \times 10^{-23} \text{ cm}^3$$

Since, H_2O molecule is spherical, if its radius is r, then volume will be

$$\frac{4}{3}\pi r^3 = 2.989 \times 10^{-23} \text{ cm}^3$$

or $\quad r^3 = 7.139 \times 10^{-24}$ cm^3
or $\quad r = (7.139 \times 10^{-24})^{1/3}$ cm $\approx 2 \times 10^{-8}$ cm
On comparing 2×10^{-8} cm with $x \times 10^{-8}$ cm
$\therefore\quad x = 2$

10. (5): The compounds which give free Cl^- ions in solution, show positive chromyl chloride test.
This test is not positive with the chlorides of Hg, Ag, Pb and Sn.

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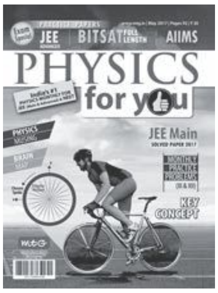

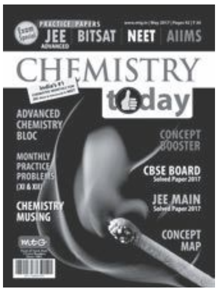

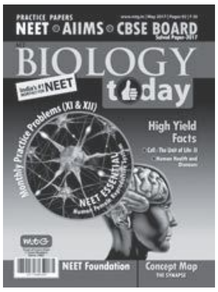

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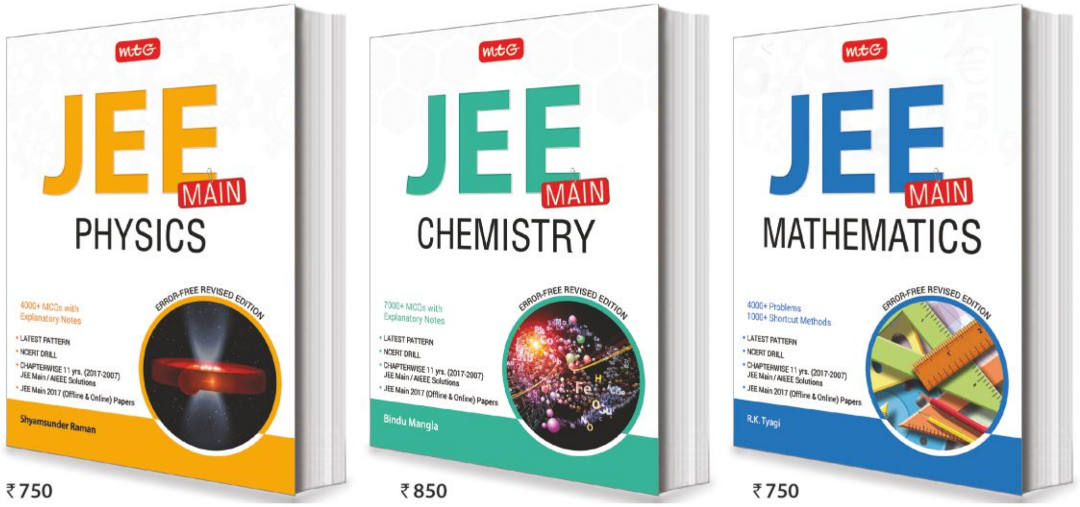
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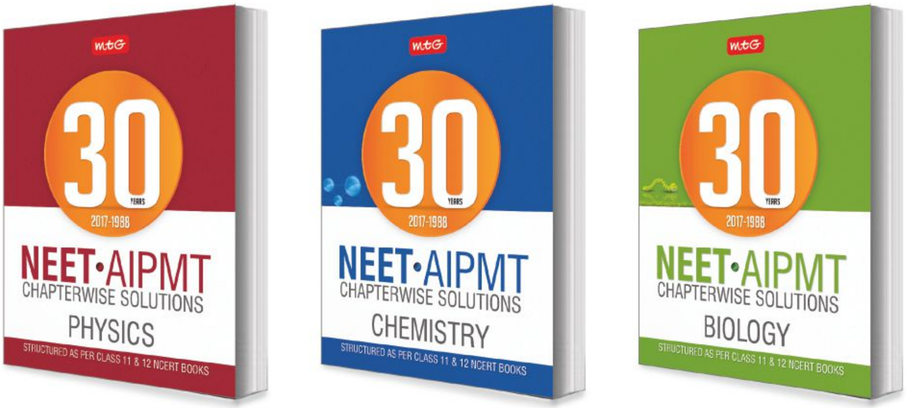
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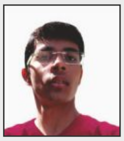
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