CHEMISTRY - 1999

PART - A

Directions : *Select the most appropriate alternative A, B, C or D in questions 1-25.*

1. The electrons, identified by quantum numbers n and l, (i) $n = 4, l = 1$, (ii) $n = 4$, $l = 0$, (iii) $n = 3, l = 2$, and (iv) $n = 3, l = 1$ can be placed in order of increasing energy, from the lowest to highest, as :
   (A) (iv) < (ii) < (iii) < (i)   (B) (ii) < (iv) < (i) < (iii)
   (C) (i) < (iii) < (ii) < (iv)   (D) (iii) < (i) < (iv) < (ii)

2. The number of neutrons accompanying the formation of $^{139}_{54}Xe$ and $^{94}_{38}Sr$ from the absorption of a slow neutron by $^{235}_{92}U$, followed by nuclear fission is :
   (A) 0   (B) 2
   (C) 1   (D) 3

3. The correct order of increasing C—O bond length of CO, CO_3^{2-}, CO_2 is :
   (A) $CO_3^{2-} < CO_2 < CO$ (B) $CO_2 < CO_3^{2-} < CO$
   (C) $CO < CO_3^{2-} < CO_2$ (D) $CO < CO_2 < CO_3^{2-}$

4. A gas will approach ideal behaviour at :
   (A) low temperature and low pressure
   (B) low temperature and high pressure
   (C) high temperature and low pressure
   (D) high temperature and high pressure

5. The normality of 0.3 M phosphorus acid (H_3PO_3) is :
   (A) 0.1   (B) 0.9
   (C) 0.3   (D) 0.6

6. The coordination number of a metal crystallizing in a hexagonal close-packed structure is :
   (A) 12   (B) 4
   (C) 8   (D) 6

7. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential of Z > Y > X, then :
   (A) Y will oxidize X and not Z   (B) Y will oxidize Z and not X
   (C) Y will oxidize both X and Z   (D) Y will reduce both X and Z.

8. The pH of 0.1 M solution of the following salts increases in the order :
   (A) $NaCl < NH_4Cl < NaCN < HCl$ (B) $HCl < NH_4Cl < NaCl < NaCN$
   (C) $NaCN < NH_4Cl < NaCl < HCl$ (D) $HCl < NaCl < NaCN < NH_4Cl$

9. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by :
   (A) temperature and pressure
   (B) temperature only
   (C) pressure only
   (D) temperature, pressure and catalyst

10. In the dichromate dianion :
    (A) 4 Cr—O bonds are equivalent
    (B) 6 Cr—O bonds are equivalent
    (C) all Cr—O bonds are equivalent
    (D) all Cr—O bonds are nonequivalent

11. One mole of calcium phosphide on reaction with excess water gives :
    (A) one mole of phosphine
    (B) two moles of phosphoric acid
    (C) two moles of phosphine
    (D) one mole of phosphorus pentoxide

12. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively, are :
    (A) $0, +1$ and -2 (B) $+2, +1$ and -2
    (C) $0, +1$ and $+2$ (D) $-2, +1$ and -2

13. On heating ammonium dichromate, the gas evolved is :
    (A) oxygen (B) ammonia
    (C) nitrous oxide (D) nitrogen

14. In the commerical electrochemical process for aluminium extraction, the electrolyte used is :
    (A) $Al(OH)_3$ in NaOH solution
    (B) an aqueous solution of $Al_2(SO_4)_3$
    (C) a molten mixture of Al_2O_3 and Na_3AlF_6
    (D) a molten mixture of $AlO(OH)$ and $Al(OH)_3$

15. The geometry of H_2S and its dipole moment are :
    (A) angular and non-zero (B) angular and zero
    (C) linear and non-zero (D) linear and zero

16. The geometry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are :
    (A) both square planar
    (B) tetrahedral and square planar, respectively
    (C) both tetrahedral
    (D) square planar and tetrahedral, respectively

17. In compounds of type ECl_3, where E = B, P, As or Bi, the angles Cl—E—Cl for different E are in the order :
    (A) $B > P = As = Bi$ (B) $B > P > As > Bi$
    (C) $B < P = As = Bi$ (D) $B < P < As < Bi$

18. In the compound $CH_2 = CH—CH_2—CH_2—C \equiv CH$, the $C_2 - C_3$ bond is of the type :

(A) $sp - sp^2$ (B) $sp^3 - sp^3$

(C) $sp - sp^3$ (D) $sp^2 - sp^3$

19. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The 'C' of CO_2 comes from :

(A) methyl group (B) carboxylic acid group

(C) methylene group (D) bicarbonate

20. The enol form of acetone, after treatment with D_2O, gives :

(A) $CH_3 — \overset{\overset{\displaystyle OD}{|}}{C} = CH_2$

(B) $CD_3 — \overset{\overset{\displaystyle O}{||}}{C} — CD_3$

(C) $CH_2 = \overset{\overset{\displaystyle OH}{|}}{C} — CH_2D$

(D) $CD_3 = \overset{\overset{\displaystyle OD}{|}}{C} — CD_3$

21. A positive carbylamine test is given by :

(A) N, N–dimethylaniline (B) 2, 4-dimethylaniline

(C) N-methyl-o-methylaniline (D) p-methylbenzylamine

22. The optically active tartaric acid is named as D (+) – tartaric acid because it has a positive :

(A) optical rotation and is derived from D-glucose

(B) pH in organic solvent

(C) optical rotation and is derived from D – (+) – glyceraldehyde

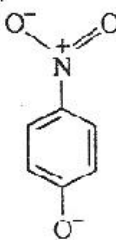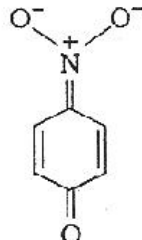(D) optical rotation only when substituted by deuterium

23. A solution of (+) –2–chloro–2–phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of :
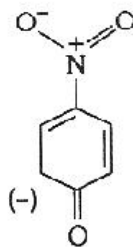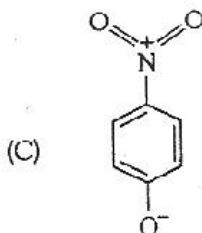
(A) carbanion (B) carbene

(C) free-radical (D) carbocation

24. The product(s) obtained via oxymercuration $(HgSO_4 + H_2SO_4)$ of 1-butyne would be :

(A) $CH_3 — CH_2 —\overset{\overset{\displaystyle O}{||}}{C}— CH_3$ (B) $CH_3—CH_2—CH_2—CHO$

(C) $CH_3—CH_2—CHO + HCHO$ (D) $CH_3—CH_2—COOH + HCOOH$
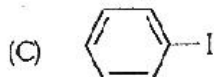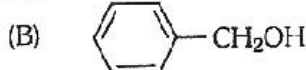
25. The most unlikely representation of resonance structures of p-nitrophenoxide ion is :

(A)

(B)

(C)

(D)

(-)

Directions : *Question numbers 26–35 carry 3 marks each and may have more than one correct answer. All correct answers must be marked to get any credit in these questions.*

26. The ether

when treated with HI produces :

(A)

(B)

(C)

(D)

27. Toluene, when treated with Br_2/Fe, gives p-bromotoluene as the major product because the CH_3 group :

(A) is *para* directing

(B) is *meta* directing

(C) activates the ring by hyperconjugation

(D) deactivates the ring

28. The following statement(s) is (are) correct :

(A) A plot of $\log K_p$ *versus* $1/T$ is linear

(B) A plot of $\log [X]$ *versus* time is linear for a first order reaction, $X \rightarrow P$

(C) A plot of $\log p$ *versus* $1/T$ is linear at constant volume

(D) A plot of p *versus* $1/V$ is linear at constant temperature

29. The following is (are) endothermic reaction(s) :

(A) Combustion of methane

(B) Decomposition of water

(C) Dehydrogenation of ethane to ethylene

(D) Conversion of graphite to diamond.

30. Ground state electronic configuration of nitrogen atom can be represented by :

(A)   (B)

(C)   (D)

31. In the depression of freezing point experiment, it is found that the :

(A) vapour pressure of the solution is less than that of pure solvent

(B) vapour pressure of the solution is more than that of pure solvent

(C) only solute molecules solidify at the freezing point

(D) only solvent molecules solidify at the freezing point

32. Ionic radii of :

(A) $Ti^{4+} < Mn^{7+}$ (B) $^{35}Cl^- < ^{37}Cl^-$

(C) $K^+ > Cl^-$ (D) $P^{3+} > P^{5+}$

33. Ammonia, on reaction with hypochlorite anion, can form :

(A) NO (B) NH_4Cl

(C) N_2H_4 (D) HNO_2

34. A buffer solution can be prepared from a mixture of :

(A) sodium acetate and acetic acid in water

(B) sodium acetate and hydrochloric acid in water

(C) ammonia and ammonium chloride in water

(D) ammonia and sodium hydroxide in water

35. An aromatic molecule will :

(A) have $4n \pi$ electrons (B) have $(4n + 2) \pi$ electrons

(C) be planar (D) be cyclic

ANSWERS

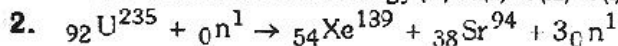|					
1. (A)	**2.** (D)	**3.** (D)	**4.** (C)	**5.** (D)	**6.** (A)
7. (A)	**8.** (B)	**9.** (A)	**10.** (B)	**11.** (C)	**12.** (A)
13. (D)	**14.** (C)	**15.** (A)	**16.** (C)	**17.** (B)	**18.** (D) ،
19. (D)	**20.** (B)	**21.** (B), (D)	**22.** (C)	**23.** (D)	**24.** (A)
25. (C)	**26.** (A), (D)	**27.** (A), (D)	**28.** (A), (B), (D)	**29.** (B), (C) (D)	**30.** (A), (D)
31. (A), (D)	**32.** (D)	**33.** (C)	**34.** (A)	**35.** (B), (C) & (D)	

SOLUTIONS

Reason of Correctness

1. On the basis of $(n + l)$ Rule   In these $(n + l)$ is lower for (ii) & (iv) but equal

(i) Value of $(n + l) = 4 + 1 = 5$ both, so in these n is minimum for (iv).

(ii) Value of $(n + l) = 4 + 0 = 4$ Hence energy order = (iv) < (ii)

(iii) Value of $(n + l) = 3 + 2 = 5$ Similaring in (i) & (iii)
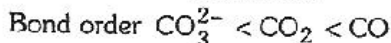
(iv) Value of $(n + l) = 3 + 1 = 4$ (iii) < (i)

Hence correct order of energy (iv) < (ii) < (iii) < (i) **Ans. (A)**

2. $_{92}U^{235} + _0n^1 \rightarrow _{54}Xe^{139} + _{38}Sr^{94} + 3_0n^1$ **Ans. (D)**

3. Bond length $\propto \dfrac{1}{\text{Bond order}}$

Bond order $CO_3^{2-} < CO_2 < CO$

Bond order in CO = 3 (with the help of molecular orbital theory)

Bond order in $CO_2 = \dfrac{\text{no. of bonds in all possible sides}}{\text{no. of resonating structure}}$ (By resonance)

$= \dfrac{4}{2} = 2$

Bond order in $CO_3^{2-} = \dfrac{4}{3} = 1.33$ (By resonance)

So order of bond length of C—O
$$CO < CO_2 < CO_3^{2-}$$
Ans. (D)

4. At higher temperature & low pressure **Ans. (C)**

5. H_3PO_3 is dibasic acid so its mole wt. = 2 × eq. wt.

∴   For it $1M = 2N$

Thus $0.3M = 0.6N$ **Ans. (D)**

6. Coordination number of a metal crystallizing in a hexagonal close-packing structure is (12). **Ans. (A)**

7. On the basis of reduction potential $(Z > Y > X)$

A spontaneous reaction will have the following characteristics :

Z reduced and X oxidised

Y reduced and X oxidised

Z reduced and Y oxidised
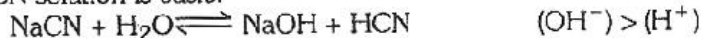
Hence   Y will oxidise X and not Z. **Ans. (A)**

8. In these HCl stronger acid.
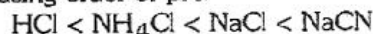
Aqueous NH_4Cl solution is slightly acidic (pH is lowest)

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl \qquad (H^+) > (OH^-)$$
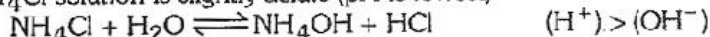
Aqueous NaCN solution is basic.

$$NaCN + H_2O \rightleftharpoons NaOH + HCN \qquad (OH^-) > (H^+)$$

Aqueous NaCl solution is **neutral.**

Hence increasing order of pH.
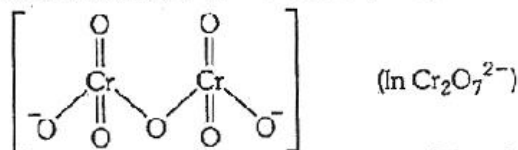
$$HCl < NH_4Cl < NaCl < NaCN$$
Ans. (B)

9. Equilibrium is effected by temperature and pressure due to change in heat as well as change in volume of substances. **Ans. (A)**

10. In the dichromate dianions, 6 Cr – O bonds are equivalent.

It shows the properties of resonance, so all six Cr-O bonds are equivalent and two bridged Cr-O bond are equivalent. **Ans. (B)**

11. $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$ **Ans. (C)**

                                 two moles

12. ON of S   in $S_8 = 0$

ON of S   in $S_2F_2 = +1$
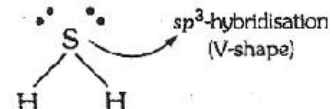
ON of S   in $H_2S = -2$ **Ans. (A)**

13. $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$ **Ans. (D)**

14. In it Na_3AlF_3 provides two functions. Hence it is used to decrease the melting point of Al_2O_3 and to increase the conductivity. **Ans. (C)**
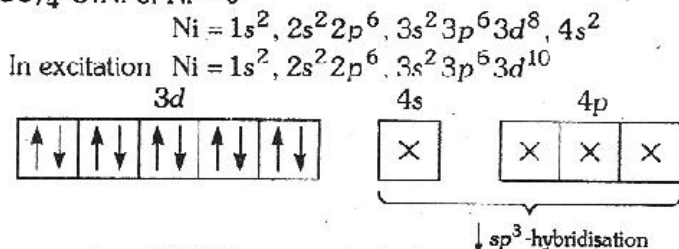
15.

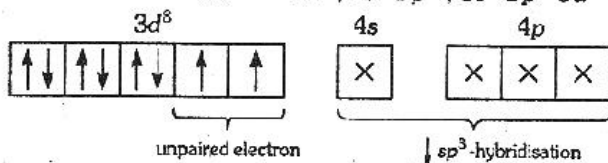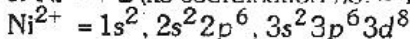Hence angular geometry of non-zero value of dipole moment. **Ans. (A)**

16. In $Ni(CO)_4$ O.N. of $Ni = 0$

$$Ni = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8, 4s^2$$

In excitation $Ni = 1s^2, 2s^2 2p^6, 3s^2 3p^5 3d^{10}$

Hence geometry of $Ni(CO)_4$ is tetrahedral.

In $Ni(PPh_3)_2Cl_2$ ON of $Ni = +2$ (Its coordination no. $= 4$)

$$Ni^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8$$

Hence geometry of $Ni(PPh_3)_2Cl_2$ is tetrahedral **Ans. (C)**

17. In BCl_3 Cl—B$\begin{matrix}Cl \\ \\ Cl\end{matrix}$ (Trigonal geometry)

sp^2-hybridisation

Bond angle $= 120°$

In PCl_3

 (Pyramidal geometry)

In $AsCl_3$

 (Pyramidal geometry)

In $BiCl_3$

 (Pyramidal geometry)
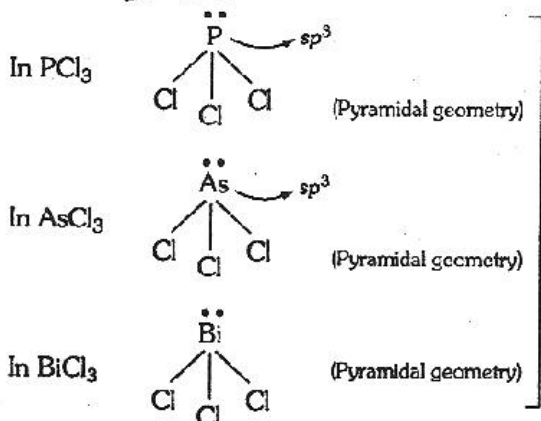
Bond angle = below $109°28'$ and decreases from PCl_3 to $BiCl_3$

In these, order of bond angle $BCl_3 > PCl_3 > AsCl_3 > BiCl_3$ **Ans. (B)**

18. $\overset{1}{CH_2} = \overset{2}{CH} — \overset{3}{CH_2} — \overset{4}{CH_2} — \overset{5}{C} \equiv \overset{6}{CH}$
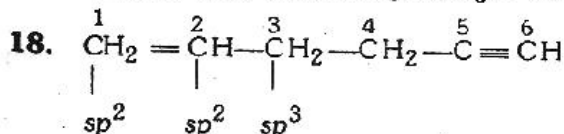
  sp^2 sp^2 sp^3

Hence C_2 and C_3 are sp^2 & sp^3-hybrid.   **Ans. (D)**

19. $C_2H_5COOH + NaHCO_3 \rightarrow C_2H_5COONa + H_2O + CO_2$ **Ans. (D)**

20. $CH_3-\underset{\underset{O-H}{|}}{C}=CH_2 \xrightarrow{D_2O} CD_3-\underset{\underset{OD}{|}}{C}=CD_2 \rightleftharpoons CD_3-\underset{\underset{O}{\|}}{C}-CD_3$ **Ans. (B)**
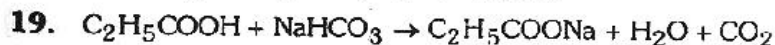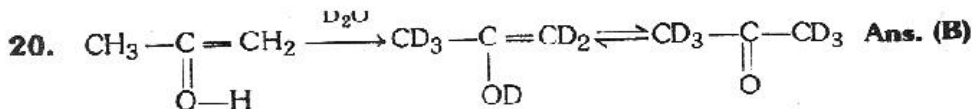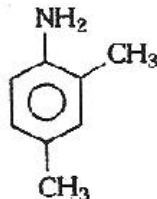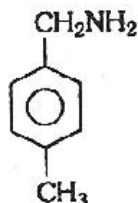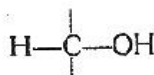
21. Carbylamine test is given by p-amines.
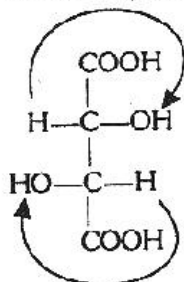
2. 4-Di methylaniline and p-methyl benzyl amine

Ans. (B) & (D)

22. D-word is used to represent the arrangement of —OH group in right side as in glyceraldehyde.

$$H-\underset{|}{\overset{|}{C}}-OH$$

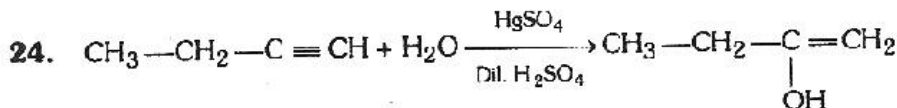and + sign is used to represent the rotation in right side. Hence in D – (+) – tartaric acid

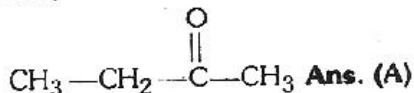Hence it has a positive optical rotation and it is derived with glyceraldehyde.

Ans. (C)
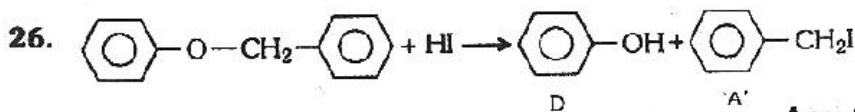
23. $SbCl_5$ is used for the formation of carbocation. **Ans. (D)**

24. $CH_3-CH_2-C\equiv CH + H_2O \xrightarrow[\text{Dil. } H_2SO_4]{HgSO_4} CH_3-CH_2-\underset{\underset{OH}{|}}{C}=CH_2$

(Because keto form is more stable than enol)

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \textbf{ Ans. (A)}$$
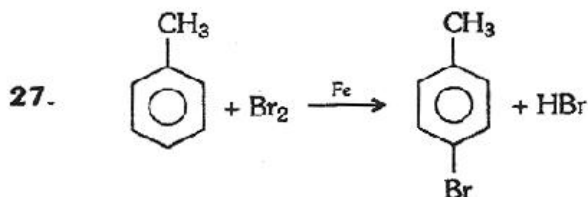
25. In structure 'C' N-atoms five bonds and (+) charged, so the structure is not possible. **Ans. (C)**

26.

Ans. (A) & (D)

27.

—CH_3 group is able to activate the benzene ring by hyperconjugation. So —CH_3 group shows *o/p*-directing influence on benzene ring. **Ans. (A) & (D)**

28. The relevant expression is as follows :

(A) $\text{Log } K_P = -\dfrac{\Delta H}{R} \cdot \dfrac{1}{T} + I$

(B) $\text{Log}(X) = \text{Log}(X_0)_0 + kt$

(C) $\dfrac{P}{t} = \text{constant}$ (at V-constant)

(d) $PV = \text{constant}$ (at T- constant)   **Ans. (A), (B) & (D) are correct.**

29. Ans. (B), (C) & (D)

30. Ans. (A) & (D)   (By Hund's Rule)

31. Ans. (A) & (D)

32. Longer the (+) charge, lower will be radii.   ∴ **Ans. (D)**

33. $2NH_3 + OCl^- \rightarrow NH_2 \cdot NH_2 + H_2O + Cl^-$ **Ans. (C)**

34. (A) & (C) are correct because a buffer solution is prepared by mixing a weak acid/base with salt of its conjugate base/acid.   **Ans. (A) & (C)**

35. An aromatic will have :

(B) $(4n + 2)\pi$ electrons   (by Huckel's Rule)

(C) planar structure   (due to resonance)

(D) cyclic structure   (due to presence of sp^2-hybrid carbon atoms).

    Ans. (B), (C) & (D)