CHEMISTRY - 1998

PART - A

1. *Read questions 1 to 28 carefully and choose from amongst the alternatives given below each question the correct lettered choice (s). A question may have one or more correct alternatives. In order to secure any marks for a given question, all correct lettered alternative(s) must be chosen.*

1. Which of the following statement(s) is(are) correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 :

(A) A deep red vapour is evolved.
(B) The vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4
(C) Chlorine gas is evolved
(D) Chromyl chloride is formed.

2. Highly pure dilute solution of sodium in liquid ammonia :

(A) shows blue colour
(B) exhibits electrical conductivity
(C) produces sodium amide
(D) produces hydrogen gas

3. The reaction $CH_3CH = CH$—C$_6$H$_4$—OH with HBr gives :

(A) $CH_3CHBrCH_2$—C$_6$H$_4$—OH
(B) $CH_3CH_2CH_2Br$—C$_6$H$_4$—OH
(C) $CH_3CHBrCH_2$—C$_6$H$_4$—Br
(D) CH_3CH_2CHBr—C$_6$H$_4$—Br

4. p-Chloroaniline and anilinium hydrochloride can be distinguished by :

(A) Sandmeyer reaction
(B) $NaHCO_3$
(C) $AgNO_3$
(D) Carbylamine test

5. The energy of an electron in the first Bohr orbit of H atom is –13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is(are) :

(A) –3.4 eV
(B) –4.2 eV
(C) -6.8 eV
(D) + 6.8 eV

6. In nitroprusside ion the iron and NO exist as Fe^{II} and NO^+ rather than Fe^{III} and NO. These forms can be differentiated by :

(A) estimating the concentration of iron
(B) measuring the concentration of CN.
(C) measuring the solid state magnetic moment
(D) thermally decomposing the compound.

7. Which of the following statement(s) is(are) correct :
(A) The coordination number of each type of ion in CsCl crystal is 8.
(B) A metal that crystallizes in bcc structure has a coordination number of 12.
(C) A unit cell of an ionic crystal shares some of its ions with other unit cells.
(D) The length of the unit cell in NaCl is 552 pm. (r_{Na^+} = 95 pm; r_{Cl^-} = 181 pm)

8. Sodium nitrate decomposes above –800°C to give :
(A) N_2 (B) O_2
(C) NO_2 (D) Na_2O

9. Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions :
(A) Fe^{3+} gives brown colour with potassium ferricyanide.
(B) Fe^{2+} gives blue precipitate with potassium ferricyanide.
(C) Fe^{3+} gives red colour with potassium thiocyanate.
(D) Fe^{2+} gives brown colour with ammonium thiocyanate.

10. Which of the following statement(s) is(are) correct :
(A) The electronic configuration of Cr is [Ar] $3d^5 4s^1$. (Atomic Number of Cr = 24).
(B) The magnetic quantum number may have a negative value.
(C) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic Number of Ag = 47)
(D) The oxidation state of nitrogen in HN_3 is –3.

11. A new carbon-carbon bond formation is possible in :
(A) Cannizzaro reaction (B) Friedel-Crafts alkylation
(C) Clemmensen reduction (D) Reimer-Tiemann reaction

12. White phosphorus (P_4) has :
(A) six P–P single bonds (B) four P–P single bonds
(C) four lone pairs of electrons (D) PPP angle of 60°.

13. Which of the following will react with water :
(A) $CHCl_3$ (B) Cl_3CCHO
(C) CCl_4 (D) $ClCH_2CH_2Cl$

14. The standard reduction potential values of three metallic cations, X, Y, Z are 0.52, –3.03 and –1.18V respectively. The order of reducing power of the corresponding metals is :
(A) Y > Z > X (B) X > Y > Z
(C) Z > Y > X (D) Z > X > Y

15. Among the following compounds, which will react with acetone to give a product containing > C = N – :
(A) $C_6H_5NH_2$ (B) $(CH_3)_3N$
(C) $C_6H_5NHC_6H_5$ (D) $C_6H_5NHNH_2$

16. Which of the following compounds will show geometrical isomerism :

(A) 2-butene (B) propene

(C) 1-phenylpropene (D) 2-methyl-2-butene

17. The geometry and the type of hybrid orbital present about the central atom in BF_3 is :

(A) linear, sp (B) trigonal planar, sp^2

(C) tetrahedral, sp^3 (D) pyramidal, sp^3

18. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with :

(A) SO_2Cl_2 (B) $SOCl_2$

(C) Cl_2 (D) NaOCl

19. Which of the following will undergo aldol condensation :

(A) acetaldehyde (B) propanaldehyde

(C) benzaldehyde (D) trideuteroacetaldehyde

20. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese :

(A) gives hardness to steel.

(B) helps the formation of oxides of iron.

(C) can remove oxygen and sulphur.

(D) can show highest oxidation state of +7.

21. Decrease in atomic number is observed during :

(A) alpha emission (B) beta emission

(C) positron emission (D) electron capture.

22. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives :

(A) diphenyl ether (B) p-hydroxyazobenzene

(C) chlorobenzene (D) benzene

23. Among the following compounds, the strongest acid is :

(A) $HC \equiv CH$ (B) C_6H_6

(C) C_2H_6 (D) CH_3OH

24. For a first order reaction :

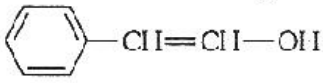
(A) the degree of dissociation is equal to $(1 - e^{-kt})$.

(B) a plot of reciprocal concentration of the reactant vs. time gives a straight line.

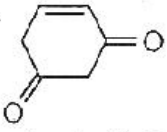
(C) the time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction.

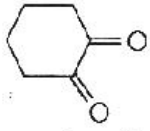
(D) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}.

25. Tautomerism is exhibited by :

(A) 

(B) 

(C) 

(D) 

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

(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) $(M_A/M_B)\,(P_B/P_A)^{1/2}$

(Where P and M are pressures and molecular weights of gases A and B respectively.)

27. For the reaction $CO(g) + H_2O(g) \quad CO_2(g) + H_2(g)$ at a given temperature the equilibrium amount of $CO_2(g)$ can be increased by :

(A) adding a suitable catalyst.
(B) adding an inert gas.
(C) decreasing the volume of the container.
(D) increasing the amount of CO (g).

28. Which of the following statement(s) is(are) correct :

(A) The pH of 1.0×10^{-8} M solution of HCl is 8.

(B) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}.

(C) Autoprotolysis constant of water increases with temperature.

(D) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point pH = (1/2) pK_a.

ASSERTION-REASON TYPE QUESTIONS

Directions : *The questions below (29 to 40) consist of an assertion in column 1 and the reason in column 2. Against the specific question number, write in the appropriate space.*

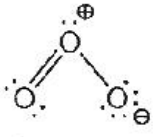
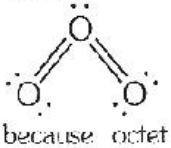
(A) If both *assertion* and *reason* are correct, and *reason* is the correct explanation of the *assertion*.

(B) If both *assertion* and *reason* are correct, but *reason* is not the correct explanation of the *assertion*.

(C) If *assertion* is correct but *reason* is incorrect.

(D) If *assertion* is incorrect but *reason* is correct.

Example :

	Assertion	Reason
	F–F bond in F_2 molecule is strong. Answer : (D)	F atom is small in size.
29.	Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.	Cyanide (CN^-) is a strong nucleophile.
30.	F atom has a less negative electron affinity than Cl atom.	Additional electrons are repelled more effectively by 3p electrons in Cl atom than by 2p electrons in F atom.
31.	Nuclide $^{30}_{13}Al$ is less stable than $^{40}_{20}Ca$.	Nuclides having odd number of protons and neutrons are generally unstable.
32.	$Al(OH)_3$ is amphoteric in nature.	Al—O and O—H bonds can be broken with equal ease in $Al(OH)_3$.
33.	The value of Van der Waals' constant 'a' is larger for ammonia than for nitrogen.	Hydrogen bonding is present in ammonia.
34.	Zn^{2+} is diamagnetic.	The electrons are lost from 4s orbital to form Zn^{2+}.
35.	Addition of Br_2 to 1 –butene gives two optical isomers.	The product contains one asymmetric carbon.
36.	The electronic structure of O_3 is 	 structure is not allowed because octet around O cannot be expanded.
37.	LiCl is predominantly a covalent compound.	Electronegativity difference between Li and Cl is too small.
38.	HNO_3 is a stronger acid than HNO_2.	In HNO_3 there are two nitrogen-to-oxygen bonds whereas in HNO_2 there is only one.
39.	Sulphate is estimated as $BaSO_4$ and not as $MgSO_4$.	Ionic radius of Mg^{2+} is smaller than that of Ba^{2+}.
40.	Acetic acid does not undergo haloform reaction.	Acetic acid has no alpha hydrogens.

ANSWERS

1. (B), (C), (D)	**2.** (A), (B)	**3.** (B)	**4.** (C)	**5.** (A)	**6.** (C)
7. (A), (C), (D)	**8.** (A), (B)	**9.** (B), (C)	**10.** (A), (B), (C)	**11.** (B), (D)	**12.** (A), (C), (D)
13. (B)	**14.** (A)	**15.** (A), (D)	**16.** (A), (C)	**17.** (B)	**18.** (C)
19. (A), (B), (D)	**20.** (A), (C)	**21.** (A), (C), (D)	**22.** (B)	**23.** (D)	**24.** (A), (D)
25. (A), (C), (D)	**26.** (C)	**27.** (D)	**28.** (B), (C)	**29.** (D)	**30.** (C)
31. (C)	**32.** (A)	**33.** (A)	**34.** (B)	**35.** (A)	**36.** (A)
37. (C)	**38.** (A)	**39.** (B)	**40.** (C)		

SOLUTIONS

Reason of correctness

1. The reactions are

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O$$

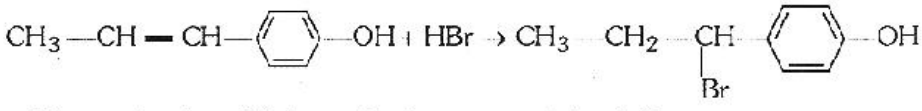
$$\underset{\text{chromyl chloride}}{CrO_2Cl_2} + 4NaOH \rightarrow \underset{\text{yellow solution}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

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

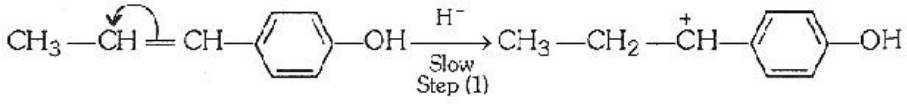
2. $Na + (x + y)\,NH_{3(l)} \rightarrow \underset{\text{Solvated cation}}{[Na(NH_3)_x]^+} + \underset{\text{Solvated electrons (Blue colour)}}{(l^- \cdot y(NH_3))^-}$

Due to formation of solvated electron it shows blue colour and electrical conductance exhibits due to both ions. **Ans. (A) & (B)**

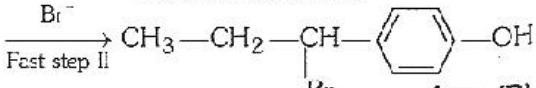
3. The reaction of $CH_3—CH=CH—C_6H_4—OH$ with HBr is given as follows.



The mechanism of this reaction is represented as follows.



carbonium (stable due to resonance)



Ans. (B)

4. Anilium hydrochloride gives the white precipitates of AgCl with $AgNO_3$.

$$C_6H_5NH_3^+Cl + AgNO_3 \rightarrow C_6H_5NH_3^+NO_3 + AgCl\downarrow$$ **Ans. (C)**

5. The energy of an electron on Bohr orbits of hydrogen atoms is given by the expression.

$$E_n = -\frac{\text{Constant}}{n^2}$$

Where n takes only integral values. For the first Bohr orbit, n = 1 and it is given that $E_1 = -13.6$ eV

$$\text{Hence } E_n = -\frac{13.6 \text{ eV}}{n^2}$$

of the given values of energy, only –3.4 eV can be obtained by substituting n – 2 in the above expression. **Ans. (A)**

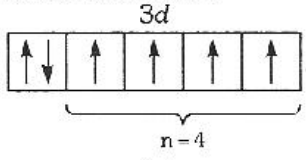
6. The magnetic moment (μ) of a species is related to its number of unpaired electrons (n) in form of following expressions.

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

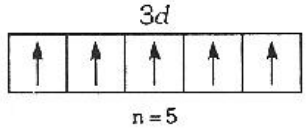
(B.M. = Bohr Magnetons)

The number of unpaired electrons in the given pairs are as follows :

$Fe^{2+} = 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^6$ or



$Fe^{3+} = 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3p^5$ or



$\overset{+}{NO}$ or $\overset{+}{\underset{\times\times}{N}}\!\!=\!\!\overset{\bullet\bullet}{O}\!:$ n = 0

NO or $\overset{\times}{\underset{\times}{N}}\overset{\times\bullet\bullet}{=\!=}O\!:$ n = 1

This given combinations differ in the number of unpaired electrons. Hence these can be differentiated by the measurement on the solid state magnetic moment of nitroprusside ion. **Ans. (C)**

7. The crystals of CsCl has body-centred cubic unit cell. Hence, each ion in this structure has coordination number of eight.

In case of crystals of NaCl two interpenetrating face-centred cubic lattices are present is these one composed entirely of Na^+ ions and the other of Cl^- ions. Each Na^+ ion is located half way between two Cl^- ions and viceversa. A unit cell of NaCl crystal has Cl^- ions at the corners as well as at the face centres and Na^+ ions are located in octahedral voids. On each edge of cubic unit cell, there are two Cl^- ions and one Na^+ ions.

$$\text{Hence } a = 2(r_{Na^-} + r_{Cl^-})$$

$$= 2(95 \text{ pm} + 181 \text{ pm}) - 552 \text{ pm}$$ **Ans. (A), (C), (D)**

8. Sodium nitrate on decomposition upto 500°C to give $NaNO_2$ and oxygen.

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2 \uparrow$$

while at higher temperature (i.e. above to 800°C) this $NaNO_2$ is decomposed into N_2O, N_2 and O_2.

$$2NaNO_2 \xrightarrow{800°C} Na_2O + 3/2\ O_2 \uparrow + N_2 \uparrow$$ **Ans. (A), (B)**

9. The blue precipitate of Fe^{2+} ions with potassium ferricyanide is due to formation of **Turnbull's blue** $K\,Fe^{II}\,[Fe^{III}\,(CN)_6]$

$$Fe^{2-} + K_3\,[Fe\,(CN)_6] \rightarrow K\,.\,Fe^{II}\,[Fe^{III}\,(CN)_6] + 2K^+$$

Potassium Ferro Ferricyanide

The red colouration of Fe^{3+} ions with potassium thiocyanate is due to the formation of $[Fe(CNS)]^{2+}$.

$$Fe^{3+} + 3KCNS \rightarrow [Fe(CNS)_3] + 3K^+$$

Ferric thiocyanate
(Red colour)

Ans. (B), (C)

10. $_{24}Cr = 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^1$

$= [Ar]\ 3d^5, 4s^1$

For magnetic quantum number (m) negative value be possible.

For s-subhell $l = 0$, hence $m = 0$

for p-subshell $l = 1$ hence $m = -1, 0, +1$

$$_{47}Ag = 1s^2, 2s^2\ 2p^6, 3s^2 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^{10}, 5s^1$$

Hence 23 electrons have aspeciesof one type and 24 of the opposite type.

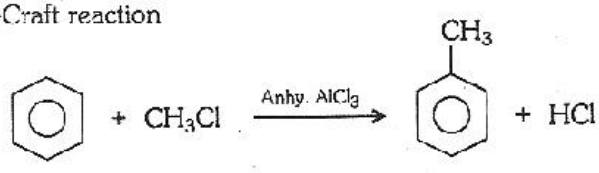
Oxidation state of N in HN_3 is $-1/3$. **Ans. (A), (B), (C)**

11. In Cannizzaro's reactions

$$2HCHO + NaOH_{(conc)} \longrightarrow CH_3OH + HCOONa$$

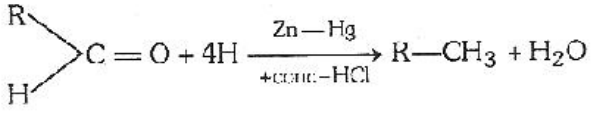
new C—C bond is not formed.

In Friedal-Craft reaction



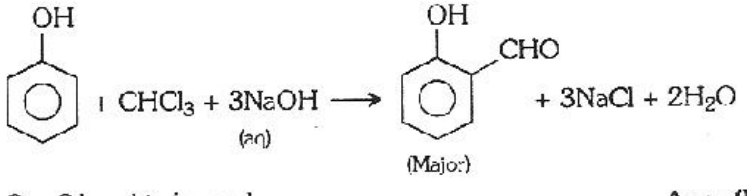
new C—C bond is formed

In Clemmenson reduction



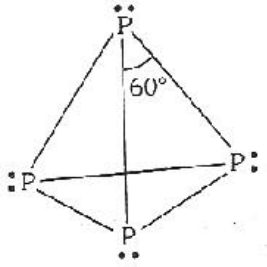
new C—C bond is not formed.

In Reimer Tiemann reactions



New C—C bond is formed. **Ans. (B), (D)**

12. The structure of P_4 is tetrahedral which is given as follows.

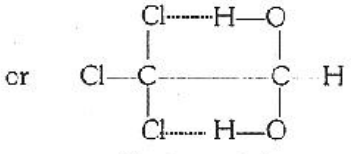


Hence six p — p single bonds, four lone pairs of electrons and P—P—P angle of 60° are present. **Ans. (A), (C), (D)**

13. CCl_3CHO reacts with water to give stable chloral monohydrate.

$$CCl_3CHO \xrightarrow{H_2O} CCl_3CH(OH)_2$$

or



chloral monohydrate

(stability is due to intramolecular H-bonding)

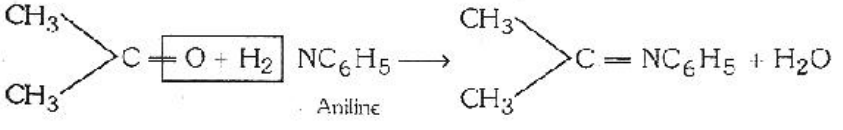
Ans. (B)

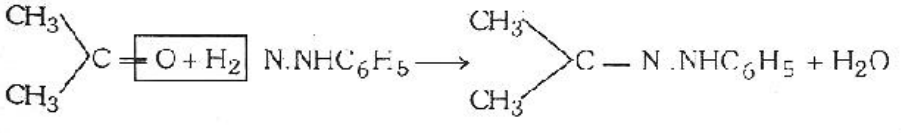
14. On decreasing the negative value of reducing electrode potential of metals, the reducing character is regularly decrease due to decreasing cation formation tendency. (i.e. electron donating tendency)

X,	Y,	Z
+0.55	−3.03	−1.18 V

Hence correct order Y > Z > X **Ans. (A)**

15. Carbonyl compound (acetone) forms condensation product with hydrazine, phenyl hydrazine aniline etc.

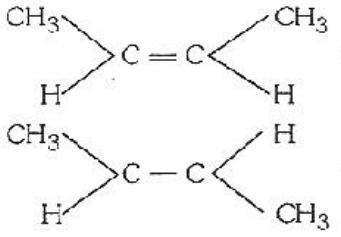




Hence in these reaction > C = N bonds are formed in products.

Ans. (A),(D)

16. $CH_3—CH=CH—CH_3$ →

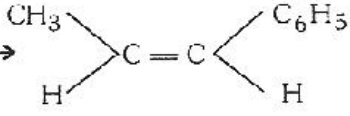


cis-isomer

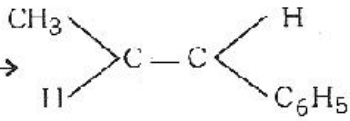
Trans-isomer

$CH_3—CH_2—CH_2—CH_3$ does not show the property of geometrical isomerism.

$CH_3—CH=CH—C_6H_5$ →



cis-isomer



Trans-isomer

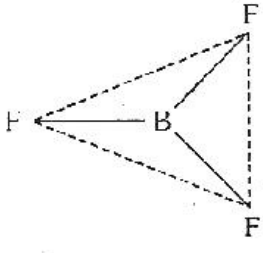
$CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH—CH_3$ does not show the property of geometrical isomerism.

Ans. (A), (C)

17. In BF_3, Boron is sp^2 – hybrid.

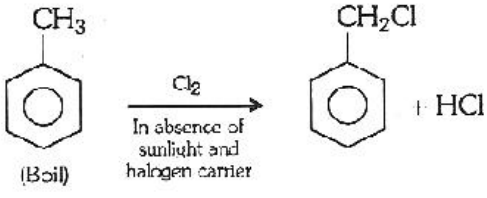
$$\underset{5}{B} = 1s^2, \underbrace{2s^1\ 2p_x^1\ 2p_y^1}_{sp^2\text{—hybridisation}}$$

These three sp^2 – hybrid orbitals are attached to each other trigonally with an angle of 120° and they are overlapped with three p-orbitals of three F-atoms on their axes. Hence the geometry of BF_3 molecule is trigonal planar.



Ans. (B)

18.



Ans. (C)

19. Those aldehydes give aldol condensation which have α-hydrogen atoms.

$$\underset{\text{All}}{2\overset{\alpha}{C}H_3-CHO} \xrightarrow[\text{Dil}]{NaOH} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO$$

Acetaldol

$$CH_3-CH_2-\overset{\beta}{C}H\boxed{O+H}-\underset{CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{Dil}]{NaOH} CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

Propanaldehyde

Benzaldehyde (C_6H_5CHO) does not have α-hydrogen atom

$$2CD_3CHO \xrightarrow[\text{Dil}]{NaOH} CD_3-\underset{OD}{\underset{|}{CH}}-CD_2CHO$$

Ans. (A), (B), (D)

20. Manganese (Mn) imparts hardness to steel as well as removes oxygen and sulphur from steel by forming slag as $MnSiO_3$.

$$Fe_2O_3 + 3Mn \rightarrow 3MnO + 2Fe$$

$$MnO + SiO_2 \rightarrow \underset{\text{(slag)}}{MnSiO_3}$$

Ans. (A), (C)

21. $${}_ZX^A \xrightarrow{-\alpha} {}_{Z-2}Y^{A-4}$$ (α-emission)

$${}_ZX^A \xrightarrow{\beta} {}_{Z+1}Z^A$$ (β-emission)

$${}_ZX^A \xrightarrow{{}_{-1}e^0} {}_{Z-1}D^A$$ (positron-emission)

$${}_ZX^m + {}_{-1}e^0 \rightarrow {}_{Z-1}D^A$$ (Electron-emission)

Ans. (A), (C), (D)

22. $$C_6H_5N_2Cl + C_6H_5OH \xrightarrow[\text{Coupling reaction}]{OH^-} C_6H_5-N=N-C_6H_4-OH$$

p-Hydroxyazobenzene

Ans. (B)

23. Order of acidic strength

$$CH_3OH > CH \equiv CH > C_6H_6 > C_2H_6$$

Although all are neutral towards the litmus paper. **Ans. (D)**

24. In first order reaction, if α is the degree of dissociation therefore

$$k = t \log_e \frac{1}{(1-\alpha)}$$

or $$kt = \log_e \frac{1}{(1-\alpha)} = -\log_e (1-\alpha)$$

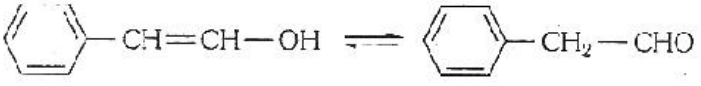
or $$e^{-kt} = 1-\alpha$$

$$\therefore \quad \alpha = \mathbf{1 - e^{kt}}$$

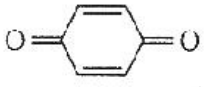
Plot of reciprocal concentration of the reactant Vs.time is linear for completion of 75%of reaction is first order, $2 \times T_{1/2}$ time is required for first order reaction dimensions of pre-exponential factor 'A' are dimensions of **k i.e.** $\mathbf{T^{-1}}$

Ans. (A), (D)

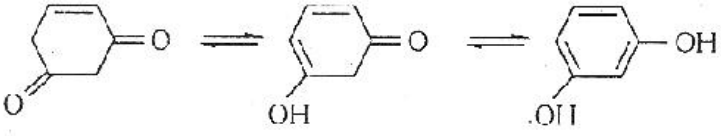
25. Tautomerism is exhibited by (A), (C), (D).

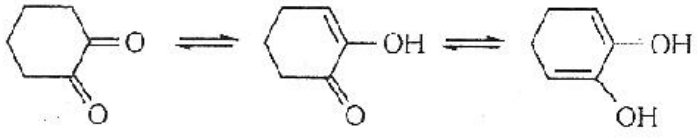


(Enol form) (Keto form)



Tautomerism is not possible





Ans. (A), (C), (D)

26. According to Graham's law of diffusion for two gases undergoing diffusion at different pressures through same hole

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \times \frac{P_A}{P_B} \quad \left(r \propto P \times \sqrt{\frac{1}{M}} \text{ At constant temperature.} \right)$$

Ans. (C)

27. $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

$$K_C = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

A catalyst simply helps in attaining the equilibrium earlier.
Addition of inert gas has no effect on a reaction because in it $\Delta n = 0$.
This equilibrium is not based upon volume because in it $\Delta n = 0$.

On increasing the amount of CO, K_C will be decreased but it is constant at constant temperature, so for maintaining the constant value of K_C, the amount of CO_2 increases. **Ans. (D)**

28. pH of 1×10^{-8} M is below to 7

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$

conjugate base of $H_2PO_4^-$ acid

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

K (Auto protolysis constant of water i.e. with ionic product of water.) increases with temperature.

For half neutralisation of a weak acid by a weak base $pH = pK_a + \log \frac{[salt]}{[acid]}$

$[Salt] = [Acid]$ $\therefore pH = pK_a$