PAPER : IIT-JAM 2005

CHEMISTRY-CY [PAPER]

NOTE: Attempt ALL the **44 questions.** Questions 1-30 **(Objective questions)** carry ***three*** marks each and questions 31-44 **(Subjective questions)** carry ***fifteen*** marks each.

1. Arrange the following in the decreasing order of acidity of the hydrogen indicated in italic

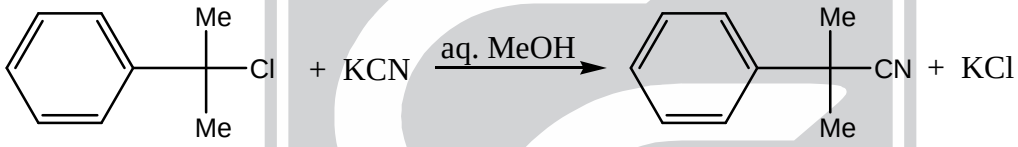
(i) $CH_3CO\underline{CH_3}$ (ii) $CH_3CO\underline{CH_2}COCH_3$

(iii) $CH_3OOC\underline{CH_2}COOCH_3$ (iv) $CH_3CO\underline{CH_2}NO_2$

(a) (ii) > (iii) > (i) > (iv) (b) (iv) > (ii) > (iii) > (i)

(c) (iv) > (iii) > (ii) > (i) (d) (ii) > (iv) > (iii) > (i)

2. For the reaction shown below if the concentration of KCN is increased four times, the rate of the reaction will be



(a) doubled (b) increased four times

(c) unaffected (d) halved.

3. Benzyl chloride is reacted with different nucleophiles shown below. Arrange them in decreasing order of reactivity.

Nucleophilies: $HO^-, CH_3COO^-, PhO^-, CH_3O^-$

(a) $CH_3O^- > HO^- > PhO^- > CH_3COO^-$ (b) $HO^- > CH_3O^- > PhO^- > CH_3COO^-$

(c) $HO^- > PhO^- > CH_3O^- > CH_3COO^-$ (d) $CH_3COO^- > CH_3O^- > HO^- > PhO^-$

4. The rate of nitration of the following aromatic compounds decreases in the order

(i) benzene (ii) pyridine (iii) thiophene (iv) toluene

(a) (iv) > (i) > (iii) > (ii) (b) (iii) > (iv) > (i) > (ii)

(c) (iii) > (ii) > (i) > (iv) (d) (ii) > (i) > (iv) > (iii)

5. The major product formed in the reaction of 1, 3-butadiene with bromine is

(a) $BrCH_2CH(Br)CH=CH_2$ (b) $CH_2=CH-CH_2CH_2Br$

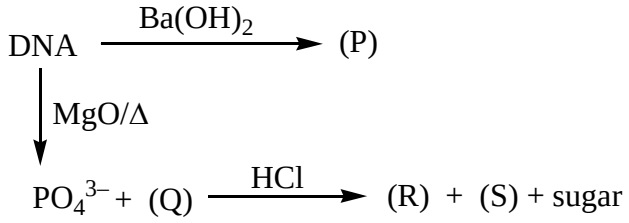
(c) $CH_2=C(Br)-C(Br)=CH_2$ (d) $BrCH_2CH=CHCH_2Br$

6. The reaction of (+) 2-iodobutane and NaI* (I* is radioactive isotope of iodine) in acetate was studied by measuring the rate of racemization (k_r) and the rate of incorporation of I*(k_i).

$$(+)CH_3CH(I)CH_2CH_3 + NaI^* \longrightarrow CH_3CH(I^*)CH_2CH_3 + NaI$$

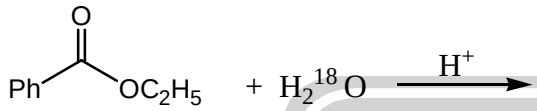
For this reaction, the relationship between k_r and k_i is:

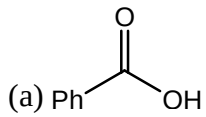
(a) $k_i = 2\times k_r$ (b) $k_i = (1/2)\times k_r$ (c) $k_i = k_r$ (d) $k_i = (1/3)\times k_r$

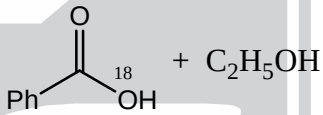
7. 

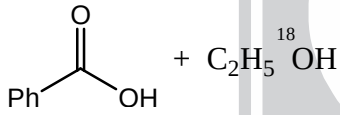
In the scheme shown above (P), (Q), (R) and (S) are
(a) (P) = purine bases, (Q) pyrimidine bases, (R) = nucleotides, (S) = nucleosides
(b) (P) = nucleosides,m (Q) = nucleotides, (R) = pyrimidine bases, (S) = purine bases.
(c) (P) = nucleosides, (Q) = nucleotides, (R) = (S) = purine bases.
(d) (P) = nucleotides, (Q) = nucleosides, (R) = pyrimidine base, (S) = purine base.

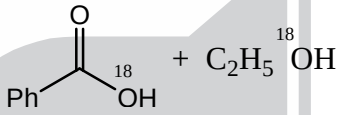
8. The products obtained from the following reaction are:



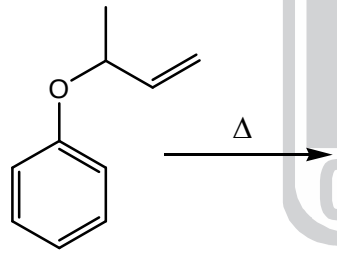
(a) 

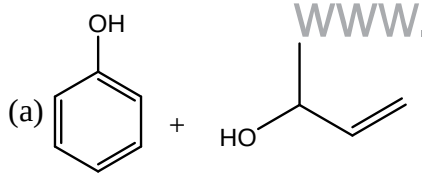
(b) 

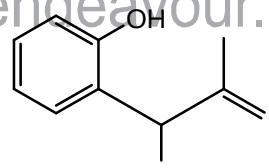
(c) 

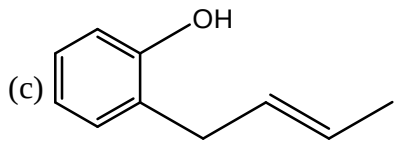
(d) 

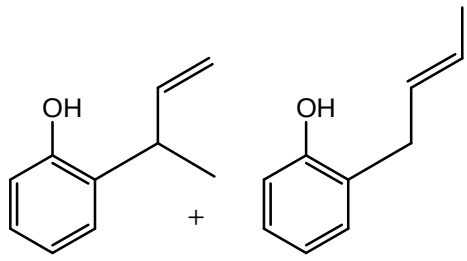
9. The product(s) obtained in the following reaction is (are)



(a) 

(b) 

(c) 

(d) 

10. Match the isoelectric point with the amino acids.

Amino acid	**Isoelectric point**
(X) H_2NCH_2COOH	(I) 9.5
(Y) $HOOCCH_2CH_2CH(NH_2)COOH$	(II) 6.0
(Z) $H_2N(CH_2)_4CH(NH_2)COOH$	(III) 3.1

(a) (X)-(II), (Y)-(III), (Z)-(I) (b) (X)-(III), (Y)-(I), (Z)-(II)
(c) (X)-(I), (Y)-(II), (Z)-(III) (d) (X)-(III), (Y)-(I), (Z)-(III)

11. The compound having the highest melting point is:
(a) LiCl (b) LiF (c) LiI (d) LiBr

12. The shape of SF_4 is:
(a) tetrahedral (b) trigonal bipyramidal
(c) square planer (d) octahedral.

13. The degree of hydration is expected to be maximum for
(a) Mg^{2+} (b) Na^{+} (c) Ba^{2+} (d) K^{+}

14. The decreasing order of the first ionization energy of the following elements is:
(a) Xe > Be > As > Al (b) Xe > As > Al > Be
(c) Xe > As > Be > Al (d) Xe > Be > Al > As

15. The radioactive isotope used to locate brain tumors is:
(a) ${}^{2}_{1}D$ (b) ${}^{15}_{7}N$ (c) ${}^{131}_{53}I$ (d) ${}^{13}_{6}C$

16. The crystal field stabilization energy of high spin d^7 octahedral complex is:
(a) $-\frac{4}{5}\Delta_0 + 2P$ (b) $-\frac{4}{5}\Delta_0 + 3P$ (c) $-\frac{9}{5}\Delta_0 + 2P$ (d) $-\frac{9}{5}\Delta_0 + 3P$

17. The complex with the most colour among the following is:
(a) $[FeF_6]^{3-}$ (b) $[MnCl_4]^{2-}$ (c) $[CoCl_4]^{2-}$ (d) $[CoF_6]^{3-}$

18. On addition of a solution of $AgNO_3$ to a solution of $Na_2S_2O_3$, it turns black on standing due to the formation of :
(a) Ag (b) Ag_2S (c) $Ag_2S_2O_2$ (d) Ag_2SO_4.

19 Among the following complexes,

(i) $[Ru(\text{bipyridyl})_3]^{+}$ (ii) $[Cr(EDTA)]^{-}$

(iii) $trans-[CrCl_2(\text{oxalate})_2]^{3-}$ (iv) $cis-[CrCl_2(\text{oxalate})_2]^{3-}$

the ones that show chirality are
(a) (i), (ii), (iv) (b) (i), (ii), (iii) (c) (ii), (iii), (iv) (d) (i), (iii), (iv)

20. The electronic configurations that have orbital angular momentum contribution in octahedral environment are
(a) d^1 and high spin d^4 (b) d^1 and d^2
(c) d^2 and high spin d^6 (d) high spin d^4 and high spin d^6.

21. For an ideal solution formed by mixing of pure liquids A and B.
(a) $\Delta H_{mixing} = 0$ (b) $\Delta H_{mixing} < 0$ (c) $\Delta H_{mixing} > 0$ (d) $\Delta S_{mixing} = 0$

22. The relationship between the equilibrium constant K_1 for the reaction:

$$CO(g)+\frac{1}{2}O_2(g)\rightleftharpoons CO_2(g)$$

and the equilibrium constant K_2 for the reaction:

$$2CO(g)+O_2(g)\rightleftharpoons 2CO_2(g)$$ is:

(a) $2K_1 = K_2$ (b) $K_1 = K_2^2$ (c) $K_1 = K_2$ (d) $K_1^2 = K_2$

23. For H-like atoms, the ground state energy is proportional to

(a) $\frac{\mu}{Z^2}$ (b) $\frac{Z^2}{\mu}$ (c) μZ^2 (d) $\frac{1}{\mu Z^2}$

Where μ is the reduced mass and Z is the nuclear charge.

24. The value of integral $\int e^{-x}x^2dx$ is

(a) $x^2e^{-x}+2xe^{-x}+2e^{-x}$ (b) $\frac{-1}{2}\left(x^2e^{-x}+2xe^{-x}+2e^{-x}\right)$

(c) $\frac{1}{2}\left(x^2e^{-x}+2xe^{-x}+2e^{-x}\right)$ (d) $-x^2e^{-x}-2xe^{-x}-2e^{-x}$

25. For the reaction $aA \rightarrow$ products, the plot of $\frac{1}{[A]}$ versus time (t) gives a straight line. Order of the reaction is:

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

26. The pH of a solution prepared from 0.005 mole of $Ba(OH)_2$ in 100 cc water is:

(a) 10 (b) 12 (c) 11 (d) 13

27. For an electron whose x-positional uncertainity is 1×10^{10} m, the uncertainity in x-component of the velocity in ms^{-1} will be of the order of (Data: $m_e = 9\times10^{-31}\ kg, h = 6.6\times10^{34}\ Js$)

(a) 10^6 (b) 10^9 (c) 10^{12} (d) 10^{15}.

28. For the following system in equilibrium, $CaCO_3(s)\rightleftharpoons CaO(s)+CO_2(g)$

the number of components, (C), phases (P) and degrees of freedom (F), respectively, are

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

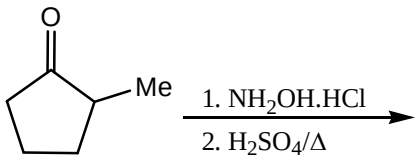
29. For the distribution of molecular velocities of gases, identify the correct order from following (where v_{mp}, v_{av}, v_{rms} are the most probable velocity, average velocity root mean square velocity, respectively):

(a) v_{rms}, v_{av}, v_{mp} (b) v_{mp}, v_{rms}, v_{av} (c) v_{av}, v_{rms}, v_{mp} (d) v_{mp}, v_{av}, v_{rms}

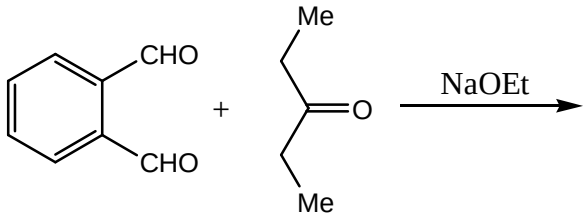
30. Given that $E^0_{Fe^{2+}/Fe} = -0.44V$ and $E^0_{Fe^{3+}/Fe^{2+}} = 0.77V$, the $E^0_{Fe^{3+}/Fe}$ is:

(a) 1.21 V (b) 0.33 V (c) –0.036 V (d) 0.036 V

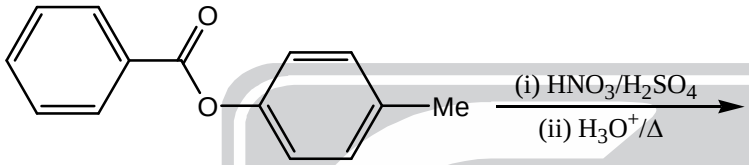
31. Identify the major product(s) formed in the following reactions. Intermediates and reaction mechanisms need not be discussed.

(a) 

[6]

(b) 

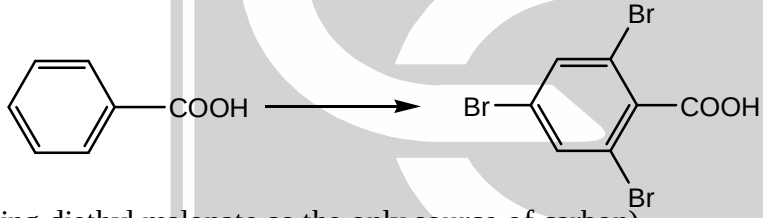
[6]

(c) 

[3]

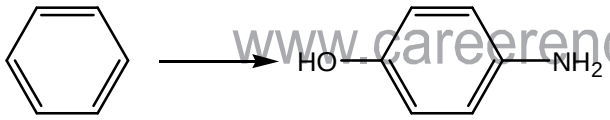
32. How may the following transformations be effected? Indicate the reagents/reaction conditions clearly in each step.

(a) (Not involving any functional group transformation of the COOH group in the starting material)



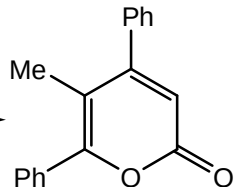
[6]

(b) (Using diethyl malonate as the only source of carbon) **[3]**

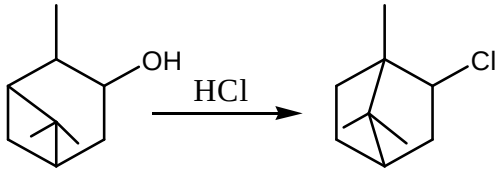
(c) 

[6]

33. Suggest a suitable mechanism for each of the following reactions.

(a) $PhCOCH_2CH_3$ + Ph—C≡C—COOEt $\xrightarrow[EtOH]{NaOEt}$ 

[6]

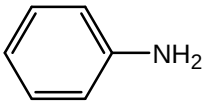
(b) 

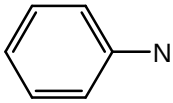
[9]

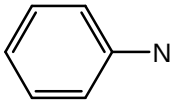
34. Rationalize the following observations using suitable mechanism.
(a) Nitration of 4 t-butyltoluene gives 4-nitrotoluene as one of the products. **[3]**
(b) cis-1-t-butylcyclohexyltrimethylammonium hydroxide undergoes Hoffmann elimination to yield 4-t-butylcyclohexene whereas the trans isomer does not (use conformations) explain.

(c) $PhMgBr + 2PhCHO \xrightarrow[2.\ \text{acid workup}]{1.\text{dry ether}} PhCOPh + PhCH_2OH$ **[6]**

35. (a) Suggest a chemical method for the separation of a mixture contain p-N, N-dimethylaminophenol and p-aminobenzoic acid and give a confirmatory test for phenol. **[6]**
(b) Write the structures of X, Y and Z in the following **[9]**

(i)  $\xrightarrow[2.\ \beta\text{-naphthol/NaOH}]{1.\ NaNO_2/\text{dil. HCl, } 0^oC}$ X

(ii)  $\xrightarrow{NaNO_2/\text{dil. HCl}}$ Y

(iii)  $\xrightarrow{NaNO_2/\text{dil. HCl}}$ Z

36. (a) Predict the hybridization and draw the structure of the following molecules based on VSEPR theory **[9]**

(i) I_3^- (ii) SO_3^{2-} (iii) $P(CH_3)_3F_2$

(b) Explain why PCl_5 exists and PH_5 does not. **[6]**

37. (a) Write balanced equations for the formation of **[6]**

(i) $P_2O_7^{-4}$ from PO_4^{-3} (ii) $\left[(H_2O)_4Fe(OH)_2Fe(OH_2)_4\right]^{4+}$ from $\left[Fe(OH_2)_6\right]^{+3}$

(b) Which one of the two solutions has lower pH? Justify your answer. **[9]**
(i) 0.1 M $Fe(ClO_4)_2$ or 0.1 M $Fe(ClO_4)_3$.
(ii) 0.1 M $Hg(NO_3)_2$ or 0.1 M $Zn(NO_3)_2$.

38. (a) Between $Co(H_2O)_6^{2+}$ and $Cu(H_2O)_6^{2+}$, which has more distorted structure and why? **[6]**

(b) Calculate CFSE (in unis of Δ_0) and spin only magnetic moment for the following complexes.

(i) $\left[CoF_6\right]^{3-}$ (ii) $\left[Fe(CN)_6\right]^{3-}$ (iii) $\left[NiCl_4\right]^{2-}$ **[9]**

39. (a) The radioactive element Ra (Z = 86) emits three alpha particles in succession. Deduce in which group the resulting element will be found? **[6]**
(b) A radioisotope sample has an initial activity of 23 dis/min. After 1/2 h, the activity is 11.5 dis/min. How many atoms of the radioactive nuclide were present originally? $\left[\alpha t_{1/2} = 0.69\right]$ **[9]**

40. (a) Write the products of the following reactions: **[9]**

(i) $CH_3I + HO^- \longrightarrow$ (ii) $CF_3I + HO^- \longrightarrow$ (iii) $2CF_3I + Na\left[Mn(CO)_5\right] \longrightarrow$

(b) Arrange BF_3, BCl_3 and BBr_3 in the increasing order of Lewis acidity and justify. **[6]**

41. Justify the following: **[15]**

(a) Considering CO_2 as an ideal gas, equipartition theorem products its total energy as 6.5 kT.

(b) ΔS for a process is the same whether the process takes place reversibly or irreversibly.

(c) The quantity ΔG equals the maximum non-expansion work done by a system in a constant temperature-pressure process.

(d) At constant temperature and pressure, $\Delta G = 0$ for a reversible phase change.

(e) Transition states cannot be isolated as independent chemical species.

42. The rate constant k for a second order reaction $P + Q \rightarrow$ products is expressed $\log_{10} k = 20 - \frac{3000}{T}$, where the concentration is in mol lit^{-1}, T is in absolute temperature and time is in minutes. The initial concentrations of both the reactants are 0.05 M. Calculate the activation energy and half life of the reaction at 27°C. (R=2 cal K^{-1} mol^{-1}). **[15]**

43. The equilibrium constant for the reaction. **[15]**

$$Fe_3O_4(s) + CO(g) \rightleftharpoons 3FeO(s) + CO_2(g)$$

at 600°C is 1.00. If a mixture intially consisting of 1 mole of Fe_3O_4, 2 moles of CO, 0.5 of FeO and 0.3 mole of CO_2 is heated to 600°C at constant total pressure of 5 atmosphere, how many moles of each substance would be present at equilibrium?

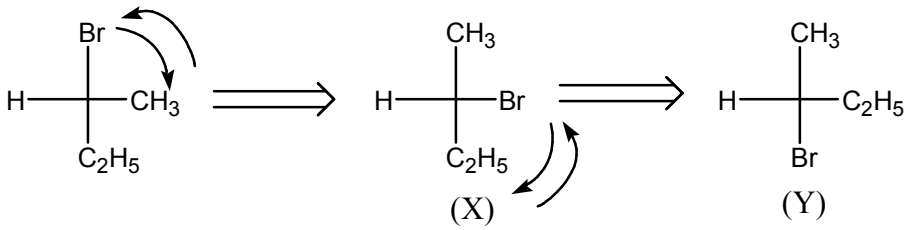
44. (a) Use the time-independent Schrodinger equation to calculate the energy of a particle of mass 'm' with V = 0 in the state $\psi = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{\pi z}{a}$ in a cubical box of length 'a'. **[9]**

(b) At 20°C, the vapour pressure of two pure liquids X and Y which form an ideal solution are 70 torr and 20 torr respectively. If the mole fraction of X in solution is 0.5, find the mole fraction of X and Y in the vapor phase in equilibrium with the solution. **[6]**

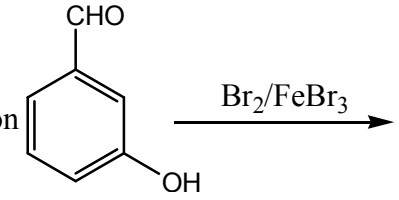
IIT-JAM Chemistry Paper-2006

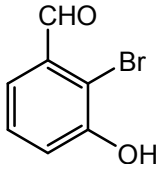
Instruction:
Q.1-30 (Objective questions) carry *three* marks each and Q.31-44 (Subjective questions) carry *fifteen* marks each.

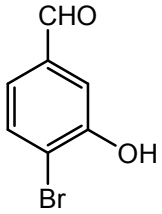
1. After the following interchanging of groups in the Fischer projection of 2-bromobutane, the configuration of (X) and (Y) will be

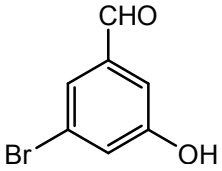


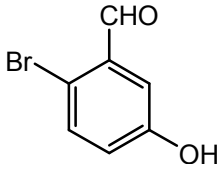
(a) X = R, Y = S
(b) X = R; Y = R
(c) X = S; Y = R
(d) X = S; Y = S

2. The major product of the reaction  is:

(a) 

(b) 

(c) 

(d) 

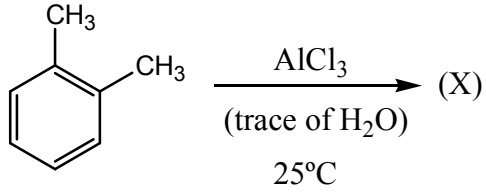
3. In the reaction sequence

$$CH_3COCH_2COOCC_2H_5 \xrightarrow[CH_3Br]{C_2H_5ONa} (X) \xrightarrow[(ii)\ H_2O/H^+]{(i)\ OH^-} (Y)$$

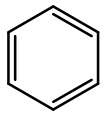
The product (Y) is:

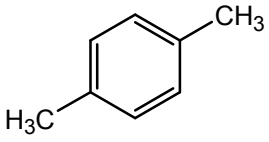
(a) $CH_3COCH_2COOCH_3$
(b) $CH_3COCH(CH_3)_2$
(c) $CH_3COCHCOOH$ (with CH_3 on the CH)
(d) $CH_3COC_2H_5$

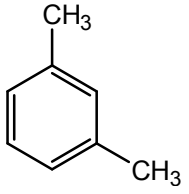
4. The major product (X) in the reaction

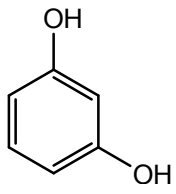


is:

(a) 

(b) 

(c) 

(d) 

5. The product of the reaction

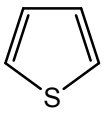
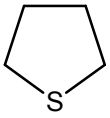
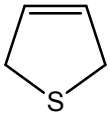
$$C_6H_6 + CO + HCl \xrightarrow[\text{heat}]{AlCl_3/Cu_2Cl_2}$$

gives positive test with Fehling's solution. The product is:

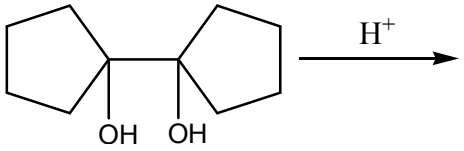
(a) C_6H_5OH (b) $C_6H_4(Cl)CHO$ (c) $C_6H_4(OH)CHO$ (d) C_6H_5CHO

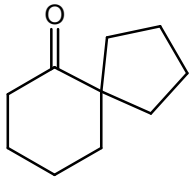
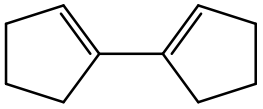
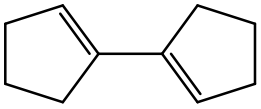
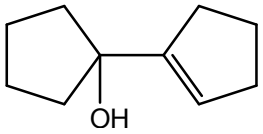
6. The compound (X) in the reaction sequence

$$\begin{matrix}CH_2COONa\\ |\\ CH_2COONa\end{matrix} \xrightarrow[\text{heat}]{P_2S_3} (X) \xrightarrow{\text{Rancy Ni}} CH_3CH_2CH_2CH_3$$

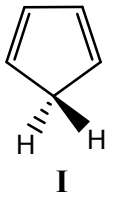
(a)  (b) $\begin{matrix}CH_2COOH\\ |\\ CH_2COOH\end{matrix}$ (c)  (d) 

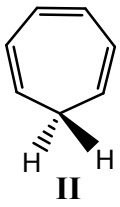
7. The major product of the reaction

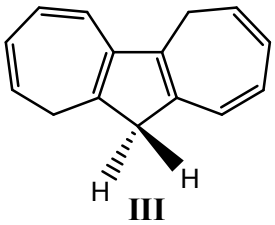


(a)  (b)  (c)  (d) 

8. The increasing order of the acidity of the hydrogen marked in **bold italics** among the following is:

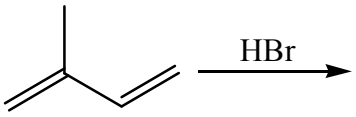

I


II

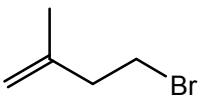
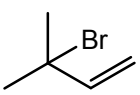
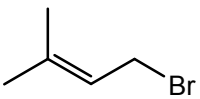
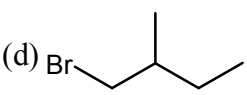

III

(a) III < II < I (b) II < I < III (c) I < II < III (d) II < III < I

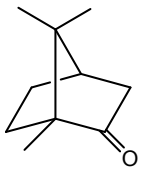
9. The major product of the reaction



is:

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

10. The number of m enantiomers of camphor



(a) Four (b) Two (c) Three (d) One

11. The decreasing order of the first ionization energy of the following elements is
(a) He > H > Be > B (b) Be > B > H > He
(c) H > He > Be > B (d) B > Be > He > H

12. If the values of Madelung constants of the following compounds are equal, then their lattice energy values decrease in the order
(a) KCl > NaF > CaO > Al_2O_3 (b) Al_2O_3 > CaO > NaF > KCl
(c) NaF > KCl > CaO > Al_2O_3 (d) Al_2O_3 > CaO > KCl > NaF

13. The fluoride, whose value of dipole moment is NOT equal to zero, is:
(a) XeF_4 (b) CF_4 (c) SF_4 (d) PF_5.

14. The decreasing order of ionic nature of the following compound is:
(a) LiI > NaBr > KCl > CsF (b) LiI > KCl > NaBr > CsF
(c) CsF > NaBr > KCl > LiI (d) CsF > KCl > NaBr > LiI

15. The atomicity and the total number of bonds in the elemental white phoshorus molecule are respectively,
(a) 4 and 6 (b) 6 and 4 (c) 4 and 4 (d) 6 and 6

16. The octahedral crystal field splitting (Δ_0) of d orbital energies of the follwoing metal ions decreases in the order
(a) $Co^{2+} > Co^{3+} > Rh^{3+}$ (b) $Rh^{3+} > Co^{3+} > Co^{2+}$
(c) $Rh^{3+} > Co^{2+} > Co^{3+}$ (d) $Co^{3+} > Co^{2+} > Rh^{3+}$

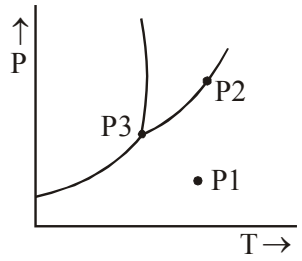
17. The half-life of a radioactive nuclide is 20 years. If a sample of this nuclide has an activity of 6400 disintegrations per minute (dis/min) today, its activity (dis/min) after 100 years would be
(a) 850 (b) 1600 (c) 200 (d) 400

18. The average value of C–C bond order in graphite is:
(a) 1 (b) 3/2 (c) 3/4 (d) 4/3

19. The optical absorption spectrum of $[Ti(H_2O)_6]^{3+}$ has its absorption maximum at 20300 cm^{-1}. The magnitude of the crystal field stabilization energy in cm^{-1} is:
(a) 8120 (b) 16240 (c) 24360 (d) 50750

20. In inorganic qualitative analysis, H_2S in acidic medium will NOT precipitate.
(a) HgS (b) ZnS (c) CuS (d) CdS

21. The phase diagram of a pure substance is sketched below.



The number of degrees of freedom at points P1, P2 and P3, respectively, are
(a) 2, 1, 0 (b) 1, 2, 0 (c) 2, 0, 1 (d) 0, 2, 1

22. The solubility products (K_{sp}) for three salts MX, MY_2 and MZ_3 are 1×10^{-8}, 4×10^{-9} and 27×10^{-8}, respectively. The solubilities of these salts follow the order
(a) MX > MY_2 > MZ_3 (b) MZ_3 > MY_2 > MX
(c) MZ_3 > MX > MY_2 (d) MY_2 > MX > MZ_3.

23. The temperature (T) dependence of the equilibrium constant (K) of a chemical reaction is correctly described by the following statement:
(a) For an endothermic reaction, the slope of ln K vs 1/T plot is positive.
(b) For an exothermic reaction, K is proportional to T.
(c) For an exothermic reaction, K at a higher temperature is lower than K at a lower temperature.
(d) If ΔH is independent of temperature, the change in K with T is smaller at lower temperatures.

24. When the concentration of K^+ across a cell membrane drops from 0.01 M to 0.001 M, the potential difference across the membrane is:
(a) 0.0 V (b) 0.0059 V (c) 0.059 V (d) 0.59 V

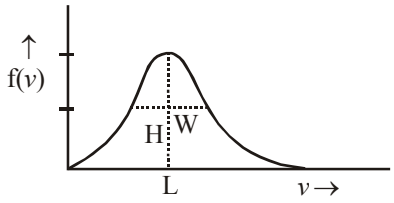
25. The statement that is correct for both electrochemical (galvanic) cells and electrolytic cells is
(a) $\Delta G = -nFE$
(b) Free energy decreases in both cells.
(c) The cell potentials are temperature independent
(d) Chemical energy is converted into electrical energy in both cells.

26. The molar heat capacity at constant volume of a colourless gas is found to be 25 $J.mol^{-1} K^{-1}$ at room temperature. The gas must be
(a) N_2 (b) O_2 (c) CO_2 (d) SO_2.

27. The wavelength for a particle (moving in a ring) is $(2\pi)^{-1/2} \exp(2i\phi)$, where ϕ is the polar angle. The probability of finding the particle in a small interval $d\phi$ when the value of $\phi = \pi / 2$ is:
(a) $d\phi$ (b) $d\phi / 2\pi$ (c) $d\phi \exp(i\pi)$ (d) $d\phi \exp(i\pi) / 2\pi$

28. An electric current of 0.965 ampere is passed for 2000 seconds through a solution containing $\left[Cu(CH_3CN)_4\right]^+$ and metallic copper is deposited at the cathode. The amount of Cu deposited is
(a) 0.005 mol (b) 0.01 mol (c) 0.02 mol (d) 0.04 mol

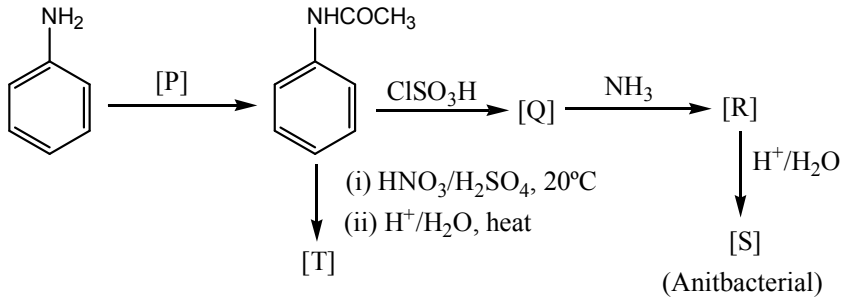
29. The Maxwell-Boltzmann distribution for molecular speeds is shown in the following figure.



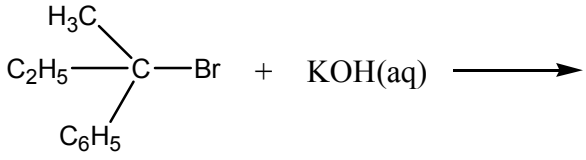
In the figure, H is the height of the peak, L is the location of the maximum and W is the width at half height. As the temperature is decreased,
(a) H increases, L deceases and W increases (b) H increases, L decreases and W decreases.
(c) H decreases, L decreases and W increases (d) H decreases, L decreases and W decreases.

30. A system undergoes two cyclic processes 1 and 2. Process 1 is reversible and process 2 is irreersible. The correct statement relating to the two processes is:
(a) ΔS (for process 1) = 0, while ΔS(for process 2) $\neq 0$
(b) $q_{cycle} = 0$ for process 1 and $q_{cycle} \neq 0$ for process 2.
(c) More heat can be converted to work in process 1 than in process 2.
(d) More work can be converted to heat in process 1 than in process 2.

31. Identify reagent (P) and write the structure of products (Q, R, S and T) in the following series of the reactions.



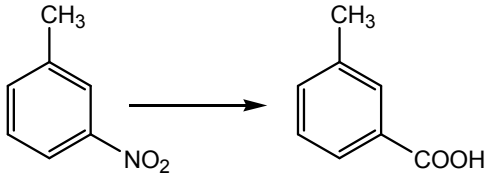
32. For the reaction



(dextro)

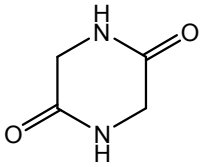
(i) What is the optical activity of the product? (ii) Draw the energy profile for the reaction
(iii) Write the structure of hte inermediate
(iv) What is the effect of the doubling concentration of KOH on the rate of the products?
(v) If aqueous KOH is replaced by alcoholic KOH. Write the structure of the products formed

33. (a) Suggest a method for the following transformation involving minimum number of steps

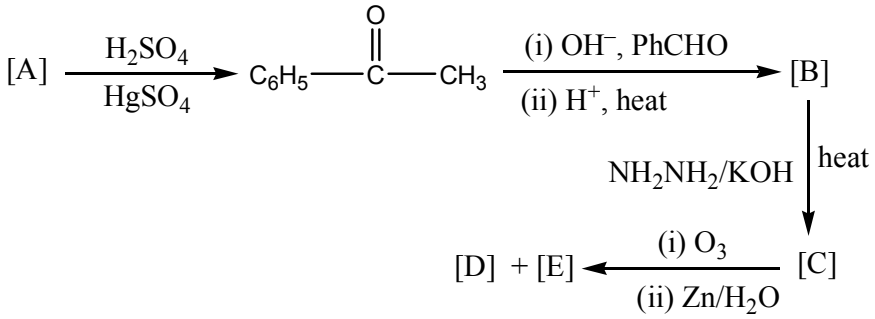


Indicate the reagents/reaction conditions required at each step clearly.

(b) A dipeptide on hydrolysis gives two amino acids (X) and (Y). If the dipeptide is first treated with HNO_2 and then hydrolysis is carried out, (X) and lactic acid are obtained. (X) on heating gives 2, 5-diketopiperazine as shown below. Identify (X) and (Y), and write their sequence in the dipeptide.



34. Identify the compounds A, B, C, D and E in the following reactions.



35. (a) Why do the boiling points of the following compounds vary in order,

$$H_2O > H_2Se > H_2S?$$

(b) Identify the products in the reaction of CCl_4 and $SiCl_4$ with water. Justify your answer.

36. (a) Write the steps involved in the production of pure elemental silicon from silica.
(b) Both the products A and B, in the following reactions, contain boron and nitrogen. Identify A and B.

$$3NH_4Cl + 3BCl_3 \xrightarrow[\text{heat}]{C_6H_5Cl} A \xrightarrow[THF]{LiAlH_4} B$$

37. (a) Addition of potassium oxalate solution to a hot solution of potassium dichromate containing dilute sulfuric acid leads to effervescence and formation of potassium trisoxalatohromate (III).
(i) Write the chemical formula of the chromium complex formed.
(ii) Write the balanced chemical formula for the formation of the complex.
(iii) Calculate the room temperature spin-only magnetic moment, in Bohr magnetons, of the complex.

(b) Write the structures of possible isomers of $\left[CoCl_2\left(en\right)_2\right]Cl$

38. (a) Draw the unit cell of CsCl lattice. Draw the (100) and (110) planes separately and indicate the positions of cesium and chloride ions.
(b) The hydration enthalpies of divalent metal ions of ten elements from calcium to zinc are plotted against their atomic numbers. Why do the hydration enthalpies of only three elements Ca, Mn and Zn fall on a straight line, whereas values for other metal ions deviate from this line.

39. (a) 5 grams of a protein was hydrolysed into amino acids, one of which is alanine. To this mixture, 0.1 gram of partially deutrated alanine, $H_2N-CH\left(CD_3\right)-COOH$, was added. After through mixing, some of the alanine was separted and purified by crystallization. The crystalline alanine contains 0.652 weight percent of D. How many grams of alanine were originally present in 5 grams of protein?
(b) What is the role of ammoniacal buffer in the volumetric titration of zinc sulphate against EDTA, using Solochrome black (Eriochrome black T) indicator? Write the structure of Zn-EDTA anionic complex.

40. (a) Calculate the pH of a solution obtained by mixing 50.00 mL of 0.20 M weak acid HA ($K_a = 10^{-5}$) and 50.00 mL of 0.20 M NaOH at room temperature.
(b) One mole of a salt of type MX is dissolved in 1.00 Kg of water. The freezing point of the solution is –2.4ºC. Calculate the percent dissociation of the salt in water.

41. (a) The rate constant of the reaction $ClO + NO \longrightarrow Cl + NO_2$ varies with temperature as:

$T(K)$	200	400
$k\left(cm^{-3}s^{-1}\right)$	2.0×10^{-11}	1.0×10^{-11}

Determine the Arrhenius activation energy of the reaction, assuming that the frequency factor does not change in this temperature range.
(b) Ozone seems to be formed in the atmosphere through the photolysis of diatomic molecule:

$$O_2 \xrightarrow[h\nu]{k_0} 2O\ ;\ O + O_2 \xrightarrow{k_1} O_3\ ;\ O_3 + O \xrightarrow{k_2} 2O_2$$

Applying steady-state approximation, determine the rate law for the formation of ozone. Show that the formation of ozone follows first order kinetics when the concentration of O_3 is extremely small.

42. (a) The reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is carried out at 300 K by mixing N_2 and H_2. The standard free energy of formation of NH_3 is –16.4 kJ/mol. After one hour of mixing, the partial pressures of N_2, H_2 and NH_3 are 50 bars, 2 bars and 200 bars, respectively. What is the reaction free energy at this stage of the reaction?

(b) Plot schematically the concentration dependence of molar conductivity of a strong electrolyte and a weak electrolyte in the same figure. The limiting ionic molar conductivities of K^+ and Cl^- are 73.5 and 76.5 $Scm^2 mol^{-1}$, respectivley. If the molar conductivity of 0.1 M KCl solution is 130.0 S cm^2 mol^{-1}, calculate the Kohlrausch's constant for KCl solution.

43. (a) The electronic wavefunction (ψ) for hydrogen atom in the 2s state is given as

$$\psi \propto \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right)$$

Determine the most probable radial distance for the electron in this state and also the position of the node (in terms of a_0).

(b) Calculate the wavelength corresponding to the lowest energy excitation of an electron confined to a one-dimensional box of length 1 nm. (Energy levels for a particle in-a-one-dimensional box are given by $E_n = n^2h^2/8ma^2$).

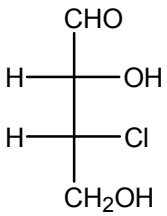
44. (a) Solve the differential equation $y'' = 5y' + 6y = 0$ with the intial conditions $y(0) = -1$ and $y'(0) = 0$. Here y' and y'' refer to the first and the second derivatives, respectively, of y with respect to x. Verify your answer.

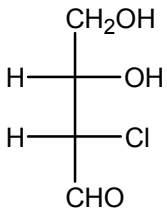
(b) For a particle with position $\vec{r} = 2\hat{i} - 3\hat{j} + \hat{k}$ and momentum $\vec{p} = \hat{i} + 2\hat{j} - 2\hat{k}$ in m and kg.m.S^{-1}, respectively, calculate the magnitude of the angular momentum $L = r \times p$

IIT-JAM Chemistry Paper-2007

Instruction:
Q.1-30 (Objective questions) carry *three* marks each and Q.31-44 (Subjective questions) carry *fifteen* marks each.

1. The compound, which
(i) Reacts rapidly with acetyl chloride
(ii) Does not react with 2, 4-dinitrophenylhydrazine and
(iii) Does not form a yellow precipitate with excess of iodine in aqueous alkali is
(a) Acetone (b) Diethyl ether (c) 2-methyl-2-propanol (d) Ethanol

2. 
1


2

The given compounds 1 and 2 are
(a) Identical (b) Diastereomeric (c) Enantiomeric (d) Constitutionally isomeric.

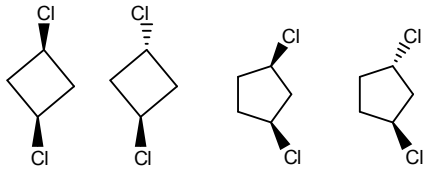
3. The correct order of dipole moments (μ) of the following componds is:

1. $CH_3CH_2CH_2CHO$ 2. $CH_3CH=CHCHO$ 3. $CH_3CH_2CH=CH_2$

(a) $\mu_1 > \mu_2 > \mu_3$ (b) $\mu_2 > \mu_3 > \mu_1$ (c) $\mu_3 > \mu_1 > \mu_2$ (d) $\mu_2 > \mu_1 > \mu_3$

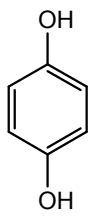
4. Which one of the following compounds gives positive test for both nitrogen and halogen with its Lassaigne's extract?
(a) $CH_3NH_2.HCl$ (b) $NH_2OH.HCl$ (c) NH_4Cl (d) $H_2NNH_2.HCl$

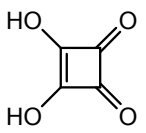
5. Which one of the following compounds is optically active?

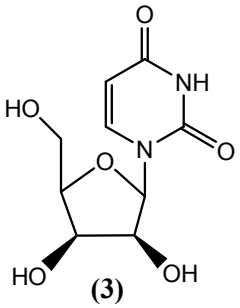

(1) **(2)** **(3)** **(4)**

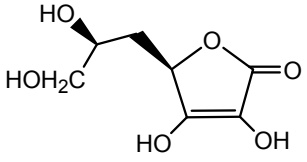
(a) 1 (b) 2 (c) 3 (d) 4

6. The compounds that react with aqueous $NaHCO_3$ to release CO_2 are


(1)


(2)

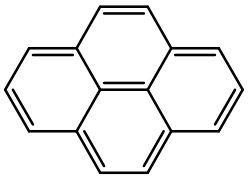

(3)


(4)

(a) 1 and3 (b) 2 and 4 (c) 2 and 3 (d) 1 and 4

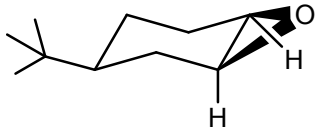
7. The complementary strand of DNA for the following single stranded DNA sequence,
5'–A–T–C–A–T–G–C–3' is:
(a) 5'–A–T–C–A–T–G–C–3' (b) 5'–T–A–G–T–A–C–G–3'
(c) 5'–G–C–A–T–G–A–T–3' (d) 5'–C–G–T–A–C–T–A–3'

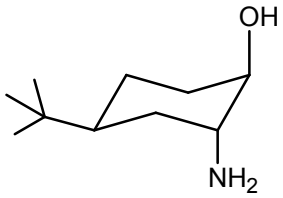
8. The value of 'n' for the following molecule according to Huckel's rule is:

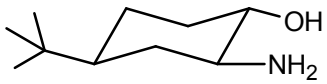


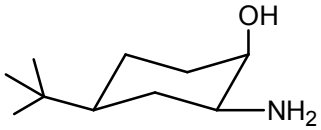
(a) 16 (b) 4 (c) 3 (d) 14

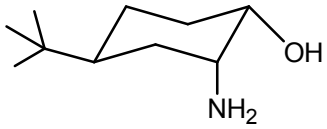
9. Which one of the following compounds reacts with nitrous acid to give the product [P]?

[P] = 

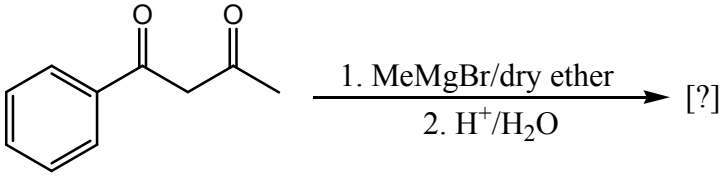
(a) 

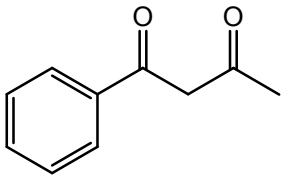
(b) 

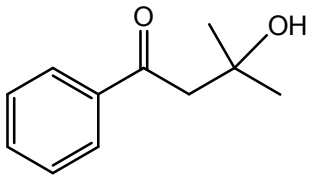
(c) 

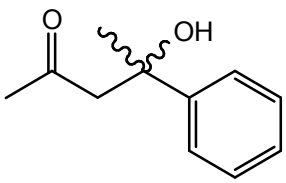
(d) 

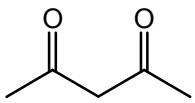
10. The main product obtained in the following reaction is:



(a) 

(b) 

(c) 

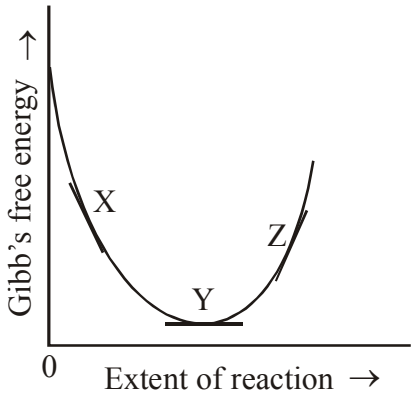
(d) 

11. For a reaction with rate equation $-dC/dt = kC^2$, C_0 and C are the concentrations of the reactant at time 0 and t respectively. If 10 minutes were required for C_0 to become $C_0/2$, the time required for C_0 to become $C_0/4$ is:
(a) 10 min (b) 20 min (c) 30 min (d) 40 min.

12. For a cyclic process performed by an ideal gas, changes in some thermodynamic functions are zero. Indicate the set in which all the functions are zero.

(a) $w, \Delta E, \Delta H, \Delta G$ (b) $q, \Delta S, \Delta H, \Delta A$ (c) $q, \Delta E, \Delta S, \Delta G$ (d) $\Delta E, \Delta S, \Delta H, \Delta A$

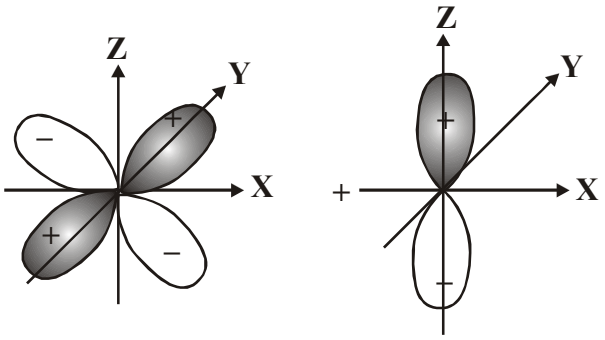
13. The plot of Gibb's free energy G and the extent of a reaction ξ is given below for the reaction $A \rightleftharpoons B$. If μ_A and μ_B are the chemical potentials of A and B respectively, the **INCORRECT** statement is:



(a) At point X, $\mu_A < \mu_B$ (b) At point Y, $\Delta G = 0$ (c) At point Z, $\mu_A > \mu_B$

(d) At equilibrium, the composition of the reaction mixture can be identified.

14. The overlap between the atomic orbitals sketched below is:



(a) Positive (b) Negative (c) Zero (d) No overalp

15. The pH of a 1.0×10^{-3} M solution of a weak acid HA is 4.0. The acid dissociation constant K_a is:

(a) 1.0×10^{-3} (b) 1.0×10^{-4} (c) 1.0×10^{-5} (d) 2.0×10^{-5}.

16. The normalisation constant 'A' for the wavefunction $\psi(\phi) = Ae^{(im\phi)}$ where $0 \le \phi \le 2\pi$ is:

(a) $\frac{1}{\sqrt{2\pi}}$ (b) $\sqrt{2\pi}$ (c) 2π (d) $\frac{1}{\sqrt{2}}$

17. The standard potential of a Daniel cell is +1.10 V and the equilibrium constant for the cell reaction is 1.5×10^{37}. It can be concluded that

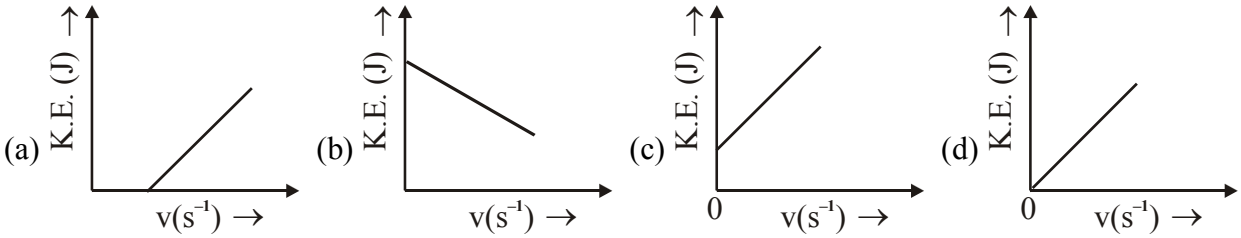
(a) Zinc oxidises copper

(b) Displacement of copper by zinc goes to near completion.

(c) Copper oxidises zinc

(d) Displacement of zinc by copper goes to completion.

18. Which one of the following figures, showing kinetic energy of the ejected electron versus the frequency (v) of the incident photon, represents the Einstein's photoelectric effect?

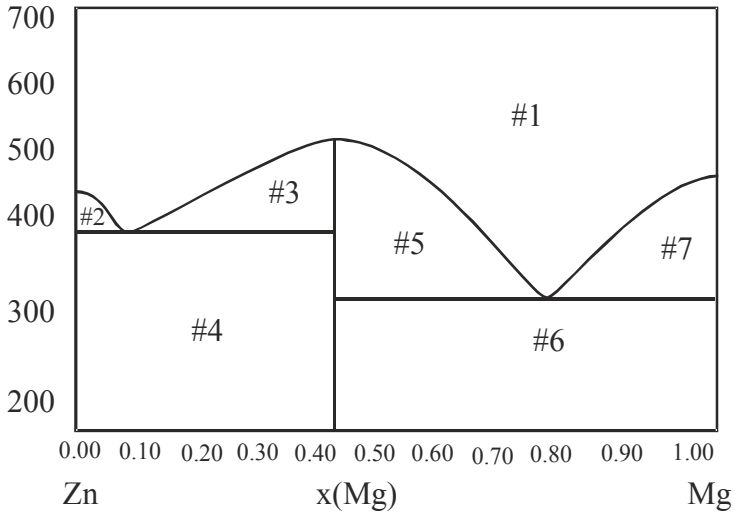


19. An aqueous solution containing 0.01 M $FeCl_3$ and 0.06 M $HClO_4$ has the same ionic strength as a solution of
(a) 0.09 M NaCl (b) 0.04 M $CuSO_4$
(c) 0.06 M $CuSO_4$ (d) 0.03 M H_3PO_4.

20. Which one of the following species is the conjugate base of HO^-?

(a) H_2O (b) O^{2-} (c) O_2^- (d) O_3^{2-}

21. The solid-liquid phase diagram for the Mg-Zn system is shown in the figure below where the vertical line at X(Mg) = 0.33 represents the formation of a congruent melting compound $MgZn_2$. The figure is divided into seven regions depending upon the physical state of the system. The composition of the region #6 represents.



(a) Single phase of a solution of Mg and Zn
(b) Two phase region between the solid Zn and solid $MgZn_2$.
(c) Two phase region between the liquid and solid $MgZn_2$.
(d) Two phase region between solid Mg and solid $MgZn_2$.

22. In the extraction of metals from their ores, which one of the following reduction methods can bring about a non-spontaneous reduction?
(a) Electrolytic reduction (b) Reduction by carbon
(c) Reduction by another metal (d) Reduction by hydrogen.

23. The correct order of the ionic radii is:

(a) $In^{3+} > Sn^{4+} > Sr^{2+} > Rb^+$ (b) $Sn^{4+} > In^{3+} > Sr^{2+} > Rb^+$

(c) $Rb^+ > In^{3+} > Sr^{2+} > Sn^{4+}$ (d) $Rb^+ > Sr^{2+} > In^{3+} > Sn^{4+}$

24. The correct valence shell electronic configuration of the element with atomic number 22 is

(a) $[Ar]4s^2 3d^2$ (b) $[Ar]3d^4$ (c) $[Ar]3d^2 4s^2$ (d) $[Ar]4s^2 4p^2$

25. The ligand with only sigma (σ) bonding character is:

(a) CN^- (b) CH_3^- (c) CO (d) NO

26. Which one of the following species is **NOT** isoelectronic with CO?

(a) N_2 (b) CN^- (c) NO^+ (d) O_2^+

27. During witting reaction, a phosphorus yield gets converted to

(a) R_3P (b) $R_3P=0$ (c) $R_3P^+HOH^-$ (d) R_2P-PR_2

28. Which of the following reactions does NOT give H_3PO_4?

(a) $Ca_3(PO_4)_2 + H_2SO_4 \longrightarrow$ (b) $P_4O_6 + H_2O \longrightarrow$

(c) $PCl_5 + H_2O \longrightarrow$ (d) $P_4S_{10} + H_2O \longrightarrow$

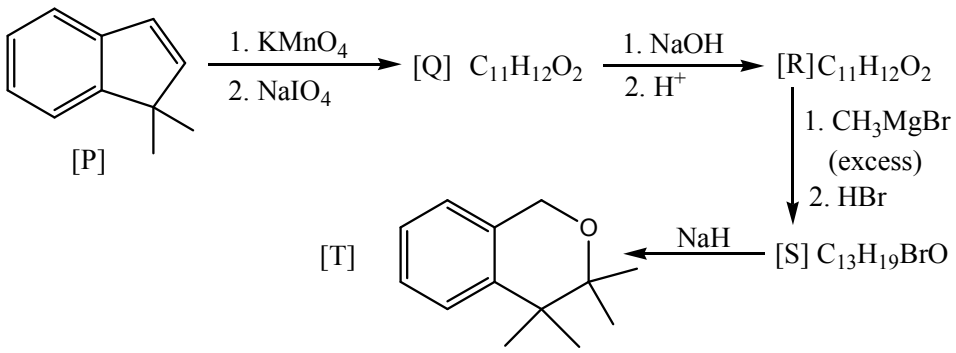
29. The ionic radii of Ca^{2+} and F^- are 100 pm and 133 pm respectively. The coordination number of Ca^{2+} in the ionic solid will be

(a) 8 (b) 6 (c) 4 (d) 2

30. The shape of CH_3^- ion is:

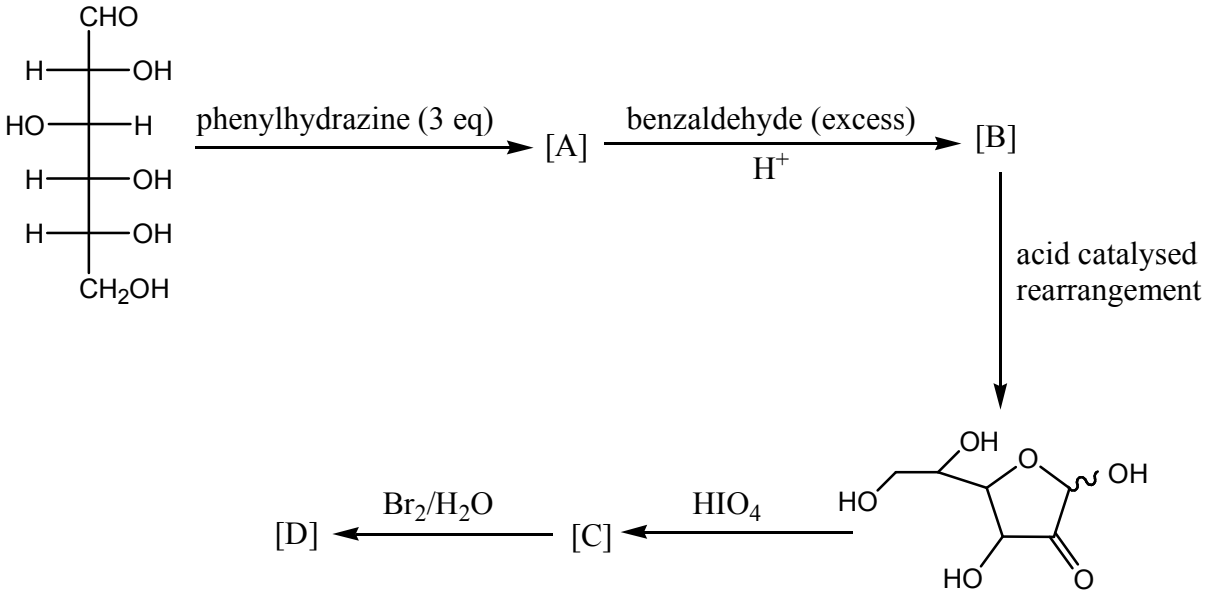
(a) trigonal planar (b) tetrahedral (c) trigonal pyramidal (d) linear.

31. Identify reagent (P) and write the structure of products (Q, S and T) in the following



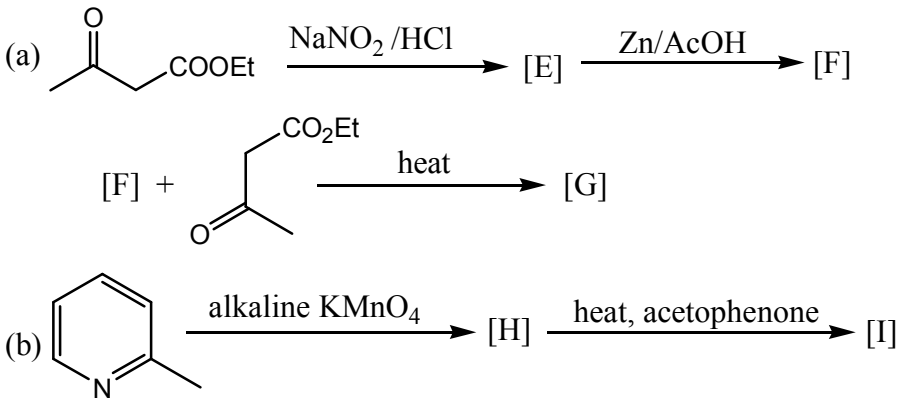
Identify the structures of the intermediate compouds Q, R and S. Show the transformation for each step

32. (a) For the following scheme of transforamations, draw the structures of A, B, C and D.

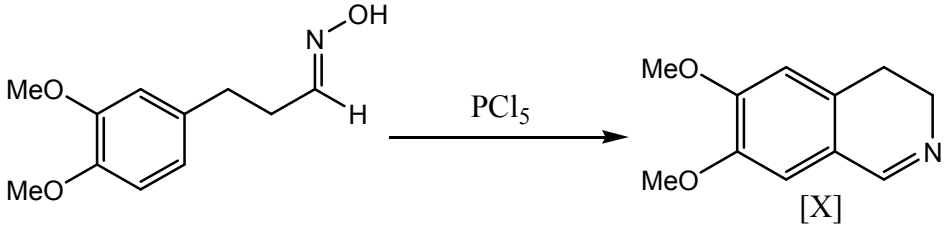


(b) Complete hydrolysis of a pentapeptide with 6 N HCl at 110ºC in a sealed tube gave 2 equivalents of glycine, one equivalent each of tyrosine, leucine and phenylalanine. Reaction of the pentapeptide with Sanger's reagent (2, 4-dinitrofluorobenzene, DNFB) and subsequent hydrolysis gave the DNFB derivative of tyrosine. Chymotrypsin cleavages of this peptide yielded tyrosine, leucine and a tripeptid. Deduce the sequence of the pentapeptide.

33. Complete the following reactions with appropriate structures for E, F, G, H and I.



34. (a) Account for the following transformation with an appropriate mechanism. Give the structure of the Hoffmann exhaustive methylation product of 1, 2-dihydro derivative of [X].



(b) The optically pure ester [J] is hydrolysed in aqueous acetic acid to form a racemic mixture of cis-4, 4-dimethyl-2-acetoxycyclopentanol [K]. Give a mechanistic explanation to account for the formation of [K] and the observed change in the optical activity.

35. (a) M is a first row transition metal. MCl_2 on treatment with aqueous ammonia gives a blue coloured solution

of complex N. A solution of MCl_2 also gives a bright red prcipitate of complex O with ethanoic dimethylglyoxime.

(i) Identify M and draw the structure of O.

(ii) Determine the hydridisation of M in complex N.

(iii) Identify the paramagnetic complex.

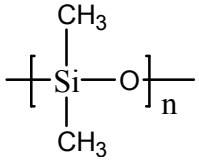
(b) $\left[Cr(H_2O)_6\right]^{3+}$ gave an absorption at 208 kJ/mol which corresponds to Δ_0. Calculate the crystal field stabilisation energy of this complex in kJ/mol.

36. (a) Consider the ethers $H_3SiOSiH_3$ and H_3COCH_3.

(i) Which ether has more lewis base character?

(ii) Which angle [Si–O–Si and C–O–C] is greater? Justify your answer.

(b) Starting from SiO_2, show how the following polymer is prepared industrially?



37. (a) A solution of metal ion $\left(M^{2+}\right)$ when treated with H_2S gas gives a black precipitate A. Precipitate **A** dissolved in hot concentrated nitric acid to give B along with elemental sulfur. The metal ion solution also gives a white precipitate C with an excess of KI. Write the chemical formulae of A, B, and C

(b) Why are potassium permanganate solutions unstable in the presence of Mn^{2+} ions? In the quantitative estimation of iron present in iron ores dissolved in dilute HCl, titrations with dichromate are preferred over titrations with permanganate. Rationalise.

38. (a) Al_2Cl_6 and Al_2Me_6 are dimeric in gas phase. Draw their structures. Which compound has more Lewis acid character? Explain.

(b) Arrange the halides $SnCl_2$, $PbCl_2$, $SiCl_2$ in increasing order of their stability. Give reasons for your answer.

39. (a) Acidification of an aqueous solution of yellow sodium chromate gives an orange coloured A. A compound solution of A on treatment with concentrated H_2SO_4 gives a bright orange solid B. Compound A in the presence of concentrated H_2SO_4 reacts with anion C to give a deep red coloured liquid. Identify A, B and C.

(b) $^{215}_{84}PO$ undergoes an α emission to give element X followed by a β emission to give element **Y**.

(i) Write the valence shell electronic configuration of Y.

(ii) Indicate the groups of the periodic table to which X and Y belong.

40. (a) When an ideal monoatomic gas is expanded from 1.5 bar, 24.8 L and 298 K into an evacuated container, the final volume becomes 49.6 L. Calculate ΔH, ΔS and ΔG for the process.

(b) The Maxwell distribution function for the distribution of speeds of molecules in gaseous systems is given by

$$f(c) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} c^2 \exp\left(\frac{-mc^2}{2kT}\right)$$

Show that the most probable speed, $c_{mps} = \left(\frac{2kT}{m}\right)^{1/2}$

41. (a) At 600 K and 200 bar, a 1:3 (molar ratio) mixture of A_2 and B_2 react to form an equilibrium mixture

containing $x_{AB_3} = 0.60$. Assuming ideal gas behaviour, calculate K_p for the reaction

$$A_2(g) + 3B_2(g) \rightleftharpoons 2AB(g)$$

(b) A 50 mL 0.05 M solution of Fe(II) is titrated with 0.05 M solution of Ce(IV) in the presence of dilute H_2SO_4 at 25ºC. Calculate the equivalence point potential and the equilibrium constant K in terms of log K.

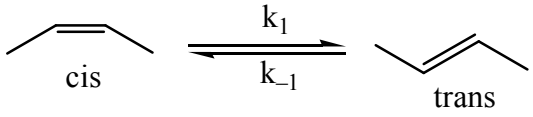
$$\left[E^0_{\left(Fe^{3+}/Fe^{2+}\right)} = +0.75\ V,\ E^0_{\left(Ce^{4+}/Ce^{2+}\right)} = +1.45V \right]$$

42. (a) The vapour pressure of D_2O at 20 ºC is 745 mm Hg. When 15 g of a non-volatile compound is dissolved in 200 g of D_2O, the pressure changes to 730 mm Hg. Assuming the applicability of Raoult's law, calculate the molecular weight of the compound.

(b) An enzyme following Michaelis-Menten kinetics was found to have highest activity at 37ºC and pH 7.0. If the maximum velocity V_{max} for this enzyme was 2.4×10^{-4} mol L^{-1} s^{-1} with an initial enzyme concentration $[E]_0 = 2.4$ nM, calculate the turnover frequency.

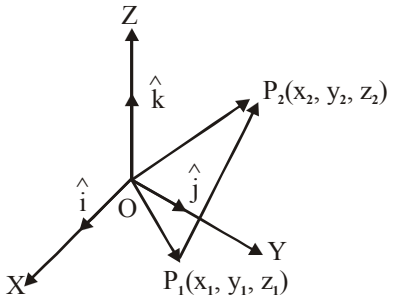
43. (a) Consider the 4π electrons in cyclobutadiene to be free particles in a 2-dimensional square box of length 2Å. Calculate the wavelength of the electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Also write down the normalised wavefunctions for the occupied degenerate states.

(b) The reaction



is first order in both directions. At 25ºC, the equilibrium constant (K) of this reaction is 0.40. If 0.115 mol. dm^{-3} of cis-isomer is allowed to equilibrate, calculate the equilibrium concentration of each isomer.

44. (a) With i, j and k as the unit vectors along, X, Y, Z axes, express the vector, $\overrightarrow{P_1P_2}$ in the given figure in terms of the coordinate of P_1 and P_2. Also determine the dot products of the unit vectors, i, j, k.



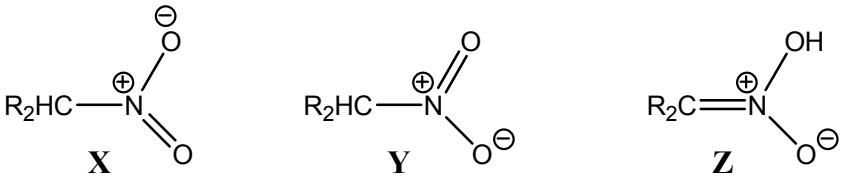
(b) Deduce whether the matrices A and B commute or not.

$$A = \begin{pmatrix} 2 & 1 \\ 0 & 1 \end{pmatrix} \qquad B = \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}$$

IIT-JAM Chemistry Paper-2008

Instruction:
Q.1-30 (Objective questions) carry *three* marks each and Q.31-44 (Subjective questions) carry *fifteen* marks each.

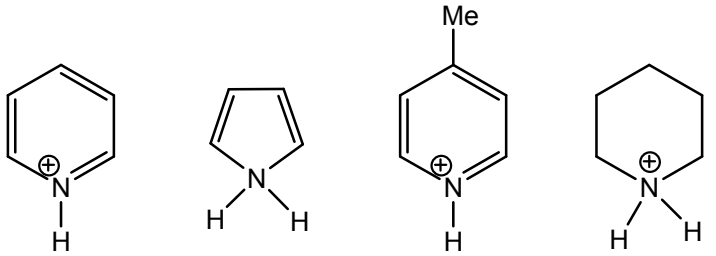
1. The correct statement describing the relationship between



is:
(a) X and Y are resonance structures and Z is a tautomer
(b) X and Y are tautomers and Z is a resonance structure.
(c) X, Y and Z are all resonance structures.
(d) X, Y and Z are all tautomers.

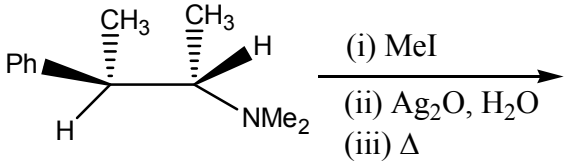
2. Among the following, the correct statement concerning the optical activity is:
(a) A molecule containing two or more chiral centres is always optically active.
(b) A molecule containing just one chiral centre is always optically active
(c) A molecule possessing alternating axis of symmetry is optically active.
(d) An optically active molecule should have at least one chiral centre.

3. The correct order of acidity among.

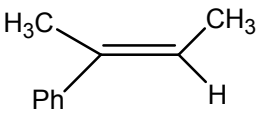


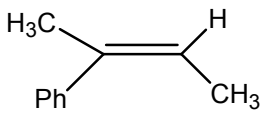
is:
(a) (i) < (ii) < (iii) < (iv)
(b) (iv) < (i) < (iii) < (ii)
(c) (ii) < (i) < (iii) < (iv)
(d) (ii) < (iv) < (i) < (iii)

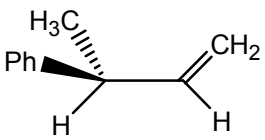
4. The major product obtained in the following reaction.

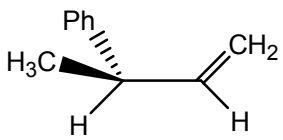


is:

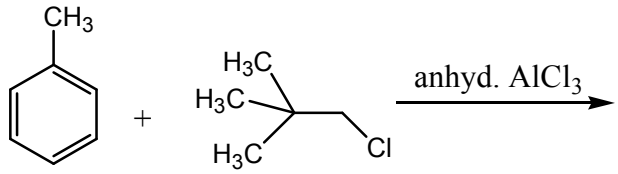
(a) 

(b) 

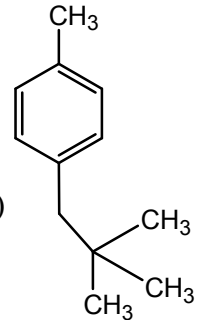
(c) 

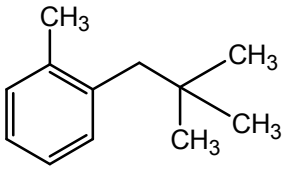
(d) 

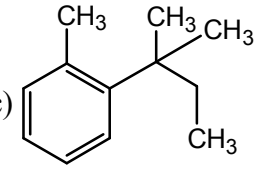
5. The major product of the following reaction

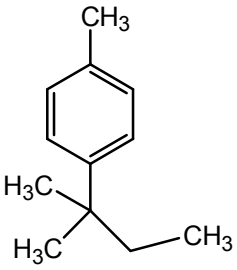


is:

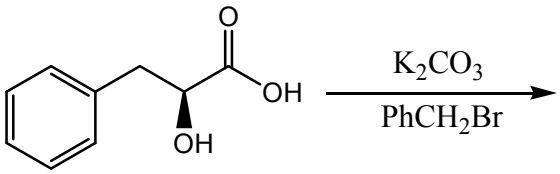
(a) 

(b) 

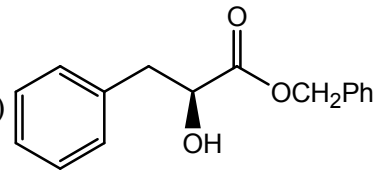
(c) 

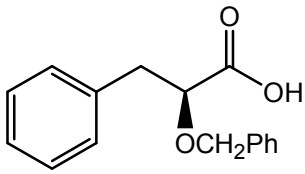
(d) 

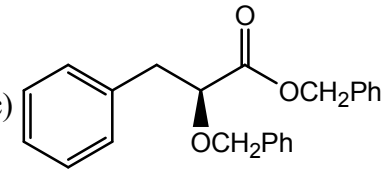
6. The major product obtained in the following reaction

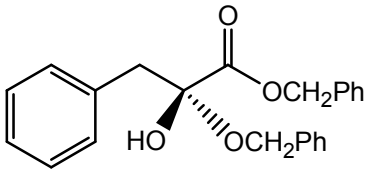


is:

(a) 

(b) 

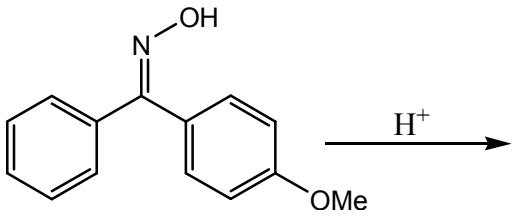
(c) 

(d) 

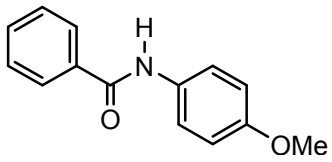
7. R–(–)–2–Bromooctane on treatment with aqueous KOH mainly gives 2-octanol that is:

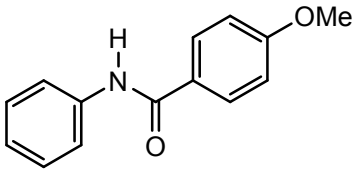
(a) Optically active with 'R' configuration
(b) Optically active with 'S' configuration
(c) A racemic mixture
(d) A meso compound

8. The major product obtained in the following reaction

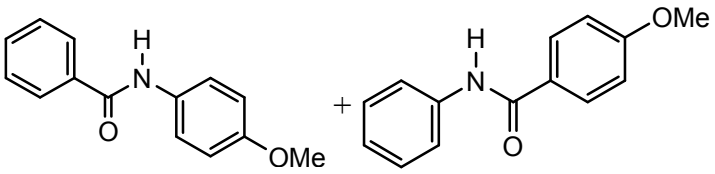


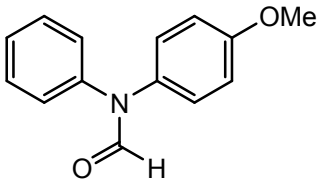
is:

(a) 

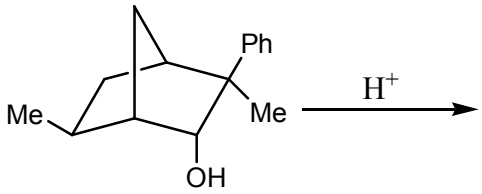
(b) 

(c) An equimolar mixture of

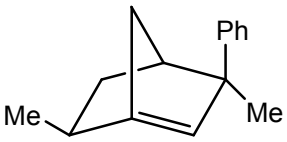


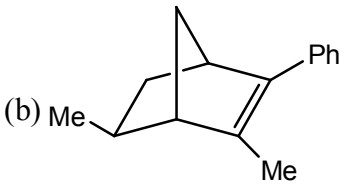
(d) 

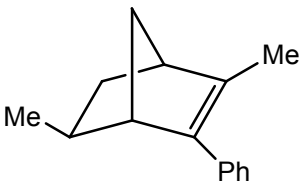
9. The major product obtained in the following reaction

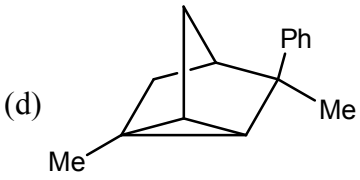


is:

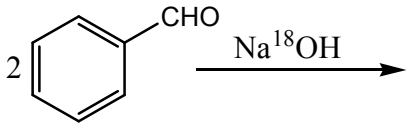
(a) 

(b) 

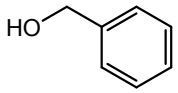
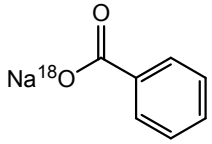
(c) 

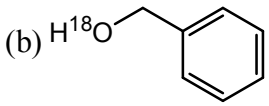
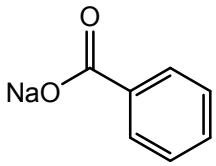
(d) 

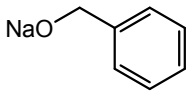
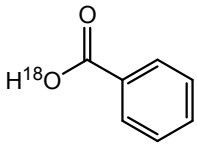
10. The products of the following reaction

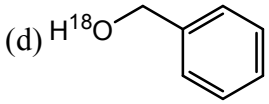
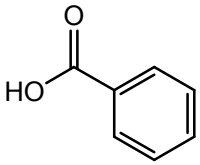


are

(a)  and 

(b)  and 

(c)  and 

(d)  and 

11. When one mole of of ice is converted to water at 0ºC and 1 atm, the work done (1 atm) is:
(a) 1.1×10^{-4} (b) 2.0×10^{-3} (c) 2.0×10^{-4} (d) 1.1×10^{-5}.

12. When 100 g of water is reversibly heated from 50ºC to 75ºC at 1 atm, the change in entropy (JK^{-1}) of the universe is:
(a) –0.31 (b) 0.31 (c) 0 (d) 3.1

13. For a zero order reaction, units of the rate constant is expressed as
(a) M^1s^{-1} (b) M^0s^{-1} (c) $M^{-1}s^{-1}$ (d) M^0s^0

14. 1×10^{-6} moles of the enzyme carbonic anhydrase dehydrates H_2CO_3 to produce 0.6 mol of CO_2 per second. The turnover number of the enzyme is:
(a) $N_A\times6\times10^{-5}$ (b) $(1/6)\times10^{-5}$ (c) $\left(6\times10^5\right)/N_A$ (d) 6×10^5

15. Given that the most probable speed of oxygen gas is 1000 ms^{-1}, the mean/average speed (ms^{-1}) under the same conditions is:
(a) 1224 (b) 1128 (c) 886 (d) 816

16. If the electron were spin 3/2 particles, instead of spin 1/2, then the number of electrons that can be accomodated in a level are
(a) 2 (b) 3 (c) 4 (d) 5

17. For a particle in a cubic box, the total number of quantum numbers needed to specify its state are
(a) 1 (b) 3 (c) 4 (d) 9

18. The maximum number of phases that can co-exist in equilibrium for a one component system is:
(a) 1 (b) 2 (c) 3 (d) 4

19. With increasing pressure, the temperature range over which the liquid state is stable.
(a) Decreases (b) Increases
(c) Remains constant (d) Decreases till the critical pressure and then increases.

20. The conductance at infinite dilution follows the order
(a) $Li^+ > Na^+ > K^+$ (b) $Na^+ > Li^+ > K^+$ (c) $K^+ > Li^+ > Na^+$ (d) $K^+ > Na^+ > Li^+$

21. The V-shape of SO_2 is due to the presence of
(a) Two $\sigma-$ and one $\pi-$ bonds.
(b) Two $\sigma-$ and two $\pi-$ bonds.
(c) Two $\sigma-$ bonds and one lone pair of electrons
(d) Two $\sigma-$ and two $\pi-$ bonds, and one lone pair of electrons.

22. The correct order of the mean bond energies in the binary hydrides is:
(a) $CH_4 > NH_3 > H_2O > HF$ (b) $NH_3 > CH_4 > H_2O > HF$
(c) $HF > H_2O > CH_4 > NH_3$ (d) $HF > H_2O > NH_3 > CH_4$

23. In CsCl structure, the number of Cs^+ ions that occupy second nearest neighbour locations of a Cs^+ ion is:
(a) 6 (b) 8 (c) 10 (d) 12

24. In the process

$$^{92}_{234}U \longrightarrow ^{230}_{90}Th + X$$

X is:

(a) α particle (b) $\beta-$particle (c) β^+-emission (d) $\gamma-$emission

25. For tetrahedral complexes, which always exhibit high spin states, the maximum CFSE (crystal field stablization energy) is:
(a) -8 Dq (b) –12 Dq (c) –16 Dq (d) –20 Dq

26. The most abundant element in earth's crust is:
(a) Aluminium (b) Iron (c) Silicon (d) Oxygen

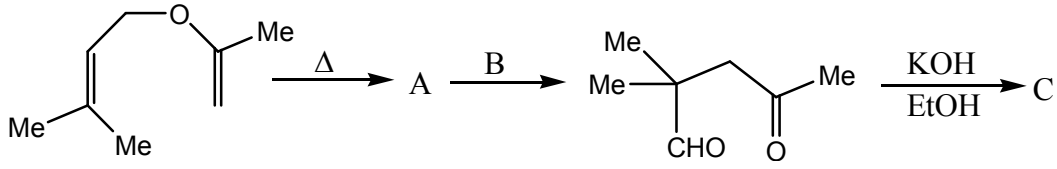
27. Metal-carbon multiple bonds in metal carbonyl are preferably identified from the stretching frequency of
(a) Carbon-oxygen bond (b) Metal-carbon bond
(c) Metal-oxygen bond (d) Carbon-carbon bond

28. In general, magntic moment of paramagnetic complexes varies with temperature as
(a) T^{2-} (b) T (c) T^2 (d) T^{-1}.

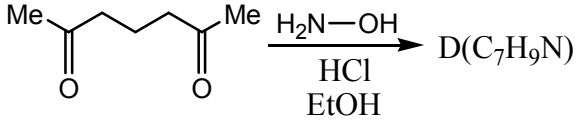
29. The compound having an S-S single bond is:
(a) $H_2S_2O_3$ (b) $H_2S_2O_4$ (c) $H_2S_2O_7$ (d) $H_2S_2O_8$

30. In a reaction, $Na_2S_2O_3$ is converted to $Na_2S_4O_6$. The equivalent weight of $Na_2S_2O_3$ for this reaction is (mol. wt. of $Na_2S_2O_3$ = M)
(a) M (b) M/4 (c) M/2 (d) M/3

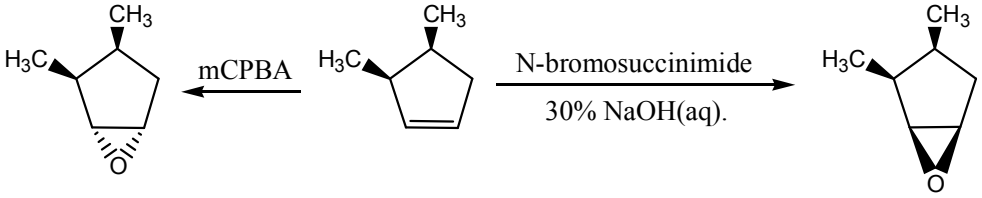
31. (a) Identify A, B and C in the following reaction sequence.



(b) Identify D in the following reaction and suggest a suitable mechanism for its formation.

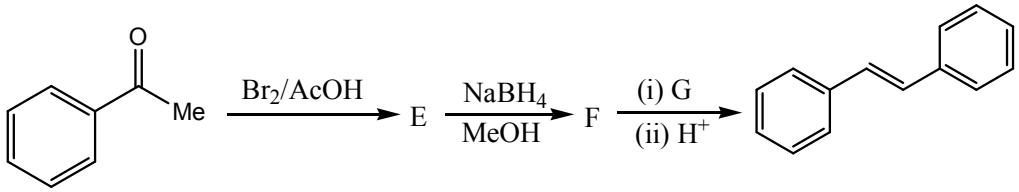


32. (a) Explain with the help of mechanisms, the observed stereoselectivity in the following epoxide formation reactions.



(b) Explain on the basis of conformational analysis why (1R, 2S)–1, 2-dimethyl-cyclohexane is optically inactive at room temperature.

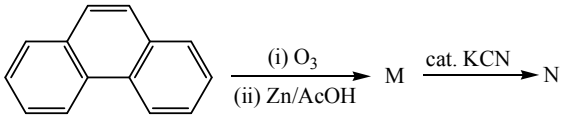
33. (a) Identify E, F and G in the following synthetic transformation:



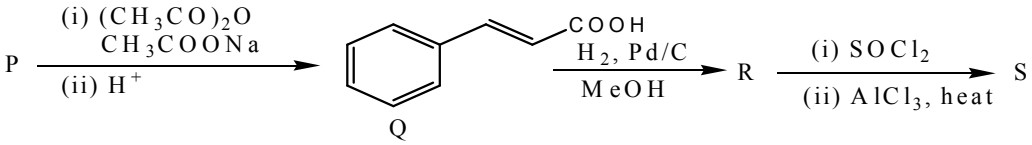
(b) An optically active compound H (C_5H_6O) on treatment with H_2 in the presence of Lindlar's catayst gave a compound I (C_5H_8O). Upon hydrogenation with H_2 and Pd/C, compound H gave J($C_5H_{12}O$). Both I and J were found to be optically inactive. Identify H, I and J.

34. (a) A disaccharide K gives a silver mirror with Tollen's reagent. Treatment of K with MeOH/HCl gives a monometry derivative L, which does not react with Tollen's reagent. Methylation of K with Me_2SO_4 and NaOH affords an octamethyl derivative of K, which upon acidic hydrolysis gives a 1:1 mixture of 2, 3, 4, 6-tetra-O-methyl-D-glucose and 2, 3, 4-tri-O-methyl-D-glucose. Disaccharide K is also hydrolysed by the enzyme maltase. Identify K and L with proper stereochemistry.

(b) Identify M and N in the following reaction sequence.



35. In the following reaction sequnce, identify P, R and S. Suggest suitable mechanism for the conversion of $P \rightarrow Q$ and $R \rightarrow S$.



36. (a) Consider the reactions.

(I) $Cr_2O_7^{2-} + H_2O_2 \xrightarrow{A} \underset{\text{Unstable}}{CrO(O_2)_2} \xrightarrow{\text{room temp.}} Cr^{3+}$

(II) $Cr^{3+} + H_2O_2 \xrightarrow{B} Cr_2O_7^{2-}$

(i) Identify A and B.

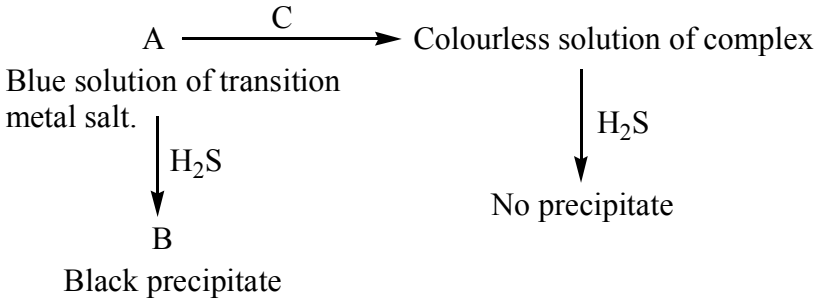
(ii) What is the role of H_2O_2 in (I) and how does A favour the formation of Cr^{3+}?

(iii) What is the role of H_2O_2 in (II) and how does B favour the formation CrO_4^{2-}?

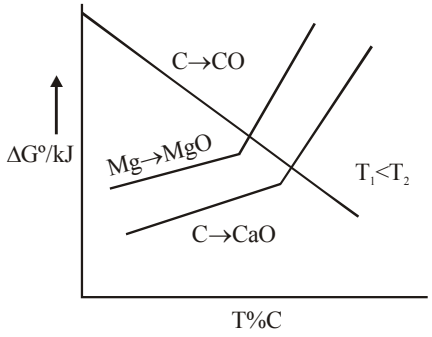
(b) With the help of equations, illustrate the role of a cis-1, 2-diol in the titration of boric acid with sodium hydroxide.

37. (a) Draw the structure of anionic Ca(II)-EDTA chelate. How many rings are formed in the chelate and specify the number of atoms in each ring?
(b) Based on VSEPR theory draw the most stable structure of ClF_3 and XeF_4.

38. (a) Identify A, B and C in the following reaction scheme



(b) From the Ellingham diagram given below, identify the metal oxide that can be reduced at a lower temperature by carbon. Justify.



39. (a) For th e complexes $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$.
(i) Show the hybridization using VB(valence bond) theory
(ii) Caculate the CFSE (crystal field stabilization energy)

(b) Identify the dark blue complex formed when $[Fe(CN)_6]^{3-}$ is treated with $FeSO_4$ and account for the origin of its colour.

40. (a) Consider the equilibrium, $A(g) \rightleftharpoons B(g) + C(g)$

At a constant pressure of 1 atm, A dissociates to the extent to the extent of 50% at 500 K. Calculate ΔG^0 (kJ mol^{-1}) for the reaction.
(b) Consider the following redox system.

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2 \qquad E^0 = 0.699\ V$$

Calculate the pH of the solution at 298 K, if the redox potential of the system is 0.817 V.

41. (a) A stream of oxygen molecules at 500 K exits from a pin-hole in an oven and strikes a slit that selects the molecules travelling in a specific direction. Given that the pressure outside the oven 2.5×10^{-7} atm, estimatethe maximum distance at which the slit must be placed from the pin-hole, in order to produce a collimated beam of oxygen. (Radius of $O_2 = 1.8\times10^{-10}$ m)
(b) Liquid water is to be circulated to transfer heat from a source to a sink at 1 atm. Considering this arrangement as a Carnot engine, calculate the maximum theoretical efficiency that can be expected from the system.

42. (a) Using Heisenberg's uncertainty principle, derive an expression for the approximate ground state energy of a particular of mass m in a one dimensional box of length L.

(b) The rate of a chemical reaction doubles when the temperature is changed from 300 K to 310 K. Calculate the activation energy (kJ mol^{-1}) for the reaction.

43. (a) Consider the reaction.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) \qquad \Delta H^0 = -606.9 \text{ kJ mol}^{-1}$$

Assuming ideal behaviour, calculate ΔU^0 when 1 mol of CH_4 is completely oxidized at STP.

(b) A photochemical reaction was carried out using monochromatic radiatin (490 nm) of intensity 100 W. When the sample was irradiated for 30 min, 0.3 mol of the reactant was decomposed. Estimate the quantum efficiency assuming 50% absorption.

44. (a) Given that

$$C_P - C_V = \frac{\alpha^2 TV}{\kappa_T} \qquad \text{where } \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{ and } \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

for a pure substance, show that $C_P - C_V = R$ for 1 mol of an ideal gas.

(b) Find the eigenvalues of the following 3×3 marix given that 2 is one of the eigenvalues. Compute the determinant of matrix **using the eigenvalues.**

$$\begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & -2 \\ 1 & -1 & 1 \end{pmatrix}$$

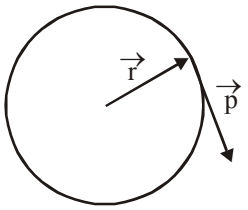
IIT-JAM Chemistry Paper-2009

Instruction:
Q.1-30 (Objective questions) carry *three* marks each and Q.31-44 (Subjective questions) carry *fifteen* marks each.

1. For an ideal gas, the plot that is NONLINEAR is:
(a) PV vs T (b) PV vs P, at constant T
(c) P vs V, at constant T (d) In P vs ln V at constant T

2. Consider two identical containers, one with 1 mole of H2 and the other with 1 mole of He. If the root-mean square (RMS) velocities of the two gases are the same, then the ratio of the temperature, $T(H_2)/T(He)$ is:
(a) 1/2 (b) 2 (c) $1/\sqrt{2}$ (d) $\sqrt{2}$

3. An electron moves around the nucleus in a circular orbit, according to the Bohr model. The radial vector $\vec{r}$ and the instaneous linear momentum vector $\vec{p}$ are shown in the diagram below.



The direction of the angular momentum vector is:
(a) along $\vec{r}$ (b) along $\vec{p}$
(c) opposite to $\vec{p}$ (d) perpendicular to both $\vec{r}$ and $\vec{p}$

4. X and Y transformed co-ordinates obtained from p and q as follows:

$$\begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} a_1 & a_3 \\ a_2 & a_1 \end{pmatrix} \begin{pmatrix} p \\ q \end{pmatrix}$$

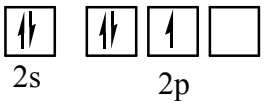
The correct set of linear equations that represent X and Y are

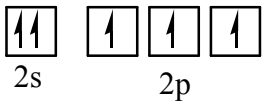
(a) $X = a_1 p + a_2 q$, $Y = a_3 p + a_4 q$ (b) $X = a_1 p + a_3 q$, $Y = a_2 p + a_4 q$ (c) $X = a_2 p + a_4 q$, $Y = a_1 p + a_3 q$ (d) $X = a_1 p + a_4 q$, $Y = a_2 p + a_3 q$

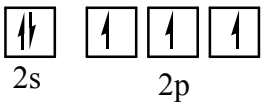
5. Which of the following is NOT a solution of the equation $\frac{d^2x}{dt^2} + \omega^2 x = 0$

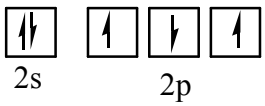
(a) $x = A\cos\omega t$ (b) $x = A\sin\omega t$ (c) $x = At^2$ (d) $x = A\left(e^{i\omega t} + e^{-i\omega t}\right)$

6. An electron is found in an orbital with one radial node and two angular nodes. Which orbital the electron is in?
(a) 1s (b) 2p (c) 3d (d) 4d

7. The acceptable valence shell electronic arrangment is:
(a) 

(b) 

(c) 

(d) 

8. If K_{sp} is the solubility product of a sparingly soluble salt A_3X_2, then its solubility is:

(a) $\left(K_{sp}/108\right)^{1/5}$ (b) $\left(K_{sp}\right)^{1/5}$ (c) $\left(K_{sp}/72\right)^{1/5}$ (d) $\left(K_{sp}\right)^{1/2}$

9. For the formation of B from A, heat liberated is 20 kJ mol^{-1}. If the activation energy for the reaction $B \rightarrow A$ is 100 kJ mol^{-1}, then the activation energy (in kJ mol^{-1}) for the reaction $A \rightarrow B$ is:

(a) 120 (b) 100 (c) 80 (d) 60

10. For the reaction $A + B \rightarrow Z$, the concentration of Z at time t is given by $[Z] = [A]_{t=0}\left(1 - e^{-kt}\right) + [Z]_{t=0}$, where k is te rate constant. The rate law is:

(a) $-\frac{d[Z]}{dt} = k[A]$ (b) $\frac{d[Z]}{dt} = k[A]$

(d) $\frac{d[Z]}{dt} = k[Z]$ (d) $\frac{d[Z]}{dt} = k[A][B]$

11. Identify the correct option:
In the priodic table, on moving from left to right along a period,
(a) The atomic size of the element increases.
(b) The first ionization potential of the element decreases.
(c) The oxide of the element becomes less basic
(d) The oxide of the element becomes more basic.

12. Among the following, the INCORRECT statement is:
(a) Diamond and graphite are two allotrops of carbon
(b) In diamond, each carbon is sp^3 hybridized.
(c) In graphite, each carbon is sp^2 hybridized
(d) Graphite shows high electrical conductivity in one direction only

13. The pH of a 1×10^{-8} M HCl solution is close to
(a) 8.0 (b) 7.1 (c) 6.9 (d) 6.0

14. The indicator phenolphthalein changes colour at $pH \sim 9$. This indicator is NOT suitable for accurate determination of the end point in the titration of

(a) CH_3COOH with NaOH (b) HCl with NH_4OH

(c) HCl with NaOH (d) HCl with KOH

15. In the thermite process, iron oxide is reduced to molten iron by aluminium powder because
(a) The melting point of iron is low (b) The reaction is highly endothermic
(c) Large amount of heat is liberated in the formation of Al_2O_3.
(d) Aluminium is an amphoteric element.

16. The number of P = O bonds present in the tetrabasic acid $H_4P_2O_7$ is:
(a) Three (b) Two (c) One (d) None

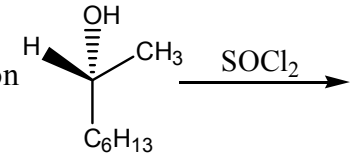
17. Egyptian blue $CaCuSi_4O_{10}$ is an example of
(a) Sheet silicate (b) Cyclic silicate (c) Pyrosilicate (d) Chain Silicate

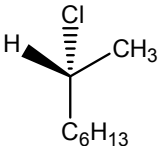
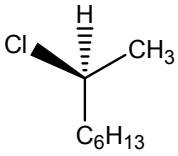
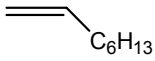
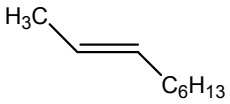
18. The formal charges on the nitrogen atom from left to right in the azide anion, $[N = N = N]^-$ are

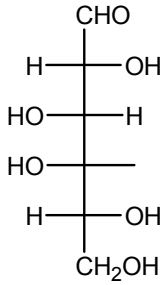
(a) +1, –1, –1 (b) –1, +1, –1 (c) –1, –1, +1 (d) –2, +1, 0

19. The unit cell of diamond can be obtained from the unit cell of
(a) ZnS (b) NaCl (c) CsCl (d) AgCl

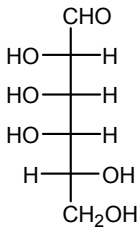
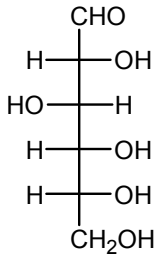
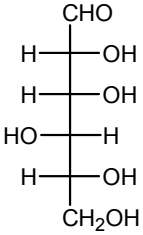
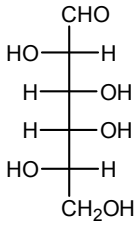
20. Calgon used for water softening is $Na_2[Na_4(PO_3)_6]$ and it is prepared by heating microscosmic salt. The microscosmic salt is:
(a) Na_2HPO_3 (b) NaH_2PO_4 (c) Na_2HPO_4 (d) $Na(NH_4)HPO_4$

21. The major product obtained in the following reaction  is:

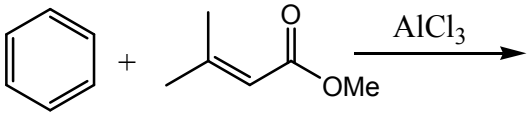
(a) 
(c) 
(c) 
(d) 

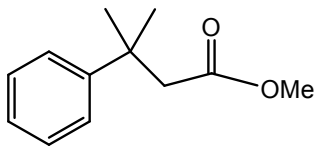
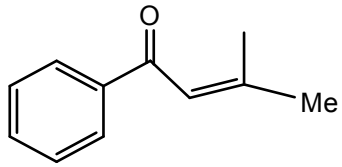
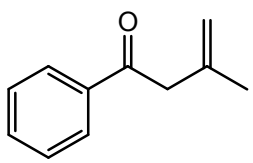
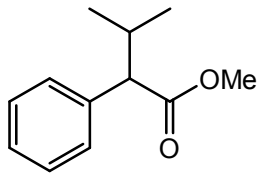
22. The strcutrure of D-galactose is 

Which one of these strucutures is L-galactose?

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

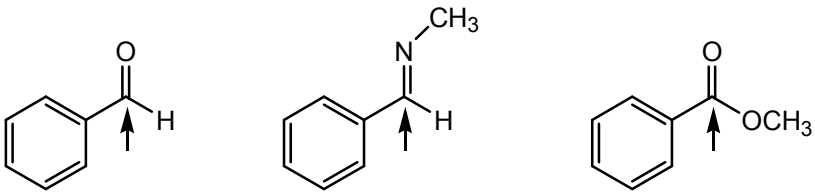
23. The maximum number of stereoisomers possible for 4-phenylbut-3-en-2ol is:
(a) 1 (b) 2 (c) 3 (d) 4

24. The major product of the reaction  is:

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

25. Which of the following is achiral?
(a) Alanine (b) Glycine (c) Proline (d) Phenylalanine

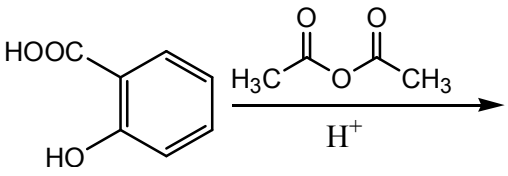
26. The reactivity order of the indicated functional groups towards a nucleophile.



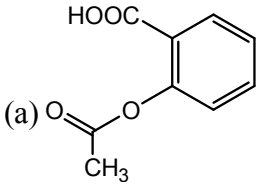
P **Q** **R**

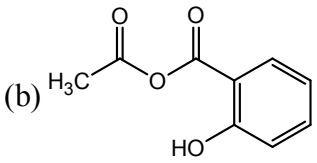
is:
(a) P > Q > R (b) Q > P > R (c) Q > R > P (d) R > P > Q

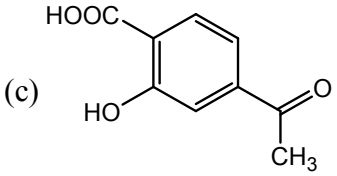
27. The major product formed in the reaction

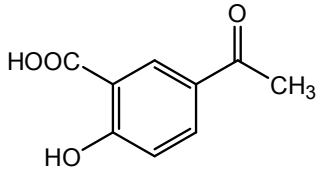


is:

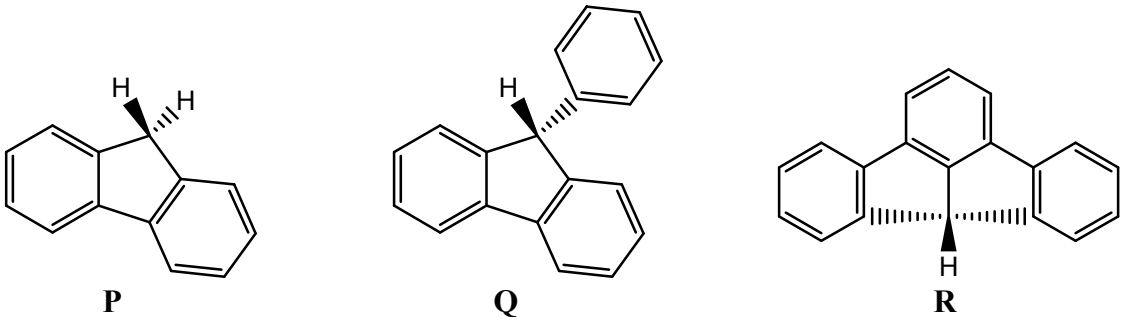
(a) 

(b) 

(c) 

(d) 

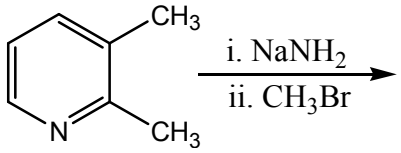
28. Arrange the following in the correct order of acidity of the hydrogen indicated in bold.

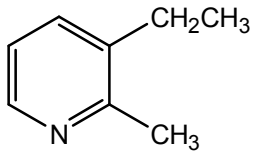


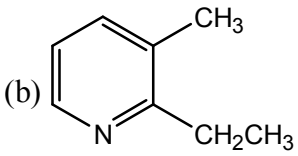
P **Q** **R**

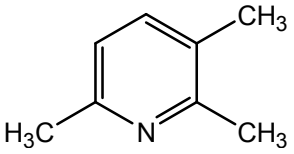
(a) P > Q > R (b) R > Q > P (c) Q > R > P (d) P > R > Q

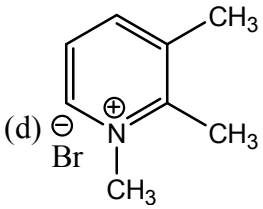
29. Among the following tlhe major product obtained in the reaction below is:



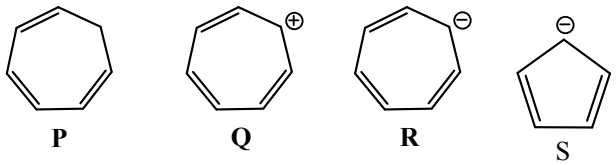
(a) 

(b) 

(c) 

(d) 

30. Which of the followng are aromatic?



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

31. (a) A conainer is partitioned into two compatments, one of which contains 2 moles of He while the other contains 3 moles of Ar. The gases are ideal. The temperature is 300 K and the pressure is 1 bar.
$R = 0.083$ L bar mol^{-1} K^{-1}, ln (2/5) = –0.92, ln (3/5) = –0.51
(i) What is the total Gibbs free energy of the two gases?
(ii) If the partition between the two compartments is removed and the gases are allowed to mix, then what is the Gibbs free energy of the mixture?
(iii) What is the change in enthalpy in this process?
(b) Obtain (i) the molar heat of formation of $CH_4(g)$ and (ii) the average C–H bond energy, to the nearest kilojoule (kJ), from the given data:

	$\Delta G\left(\text{kJ mol}^{-1}\right)$
(1) $CH_4(g) \rightarrow CH_3(g) + H(g)$	435
(2) $CH_3(g) \rightarrow CH_2(g) + H(g)$	444
(3) $CH_2(g) \rightarrow CH(g) + H(g)$	444
(4) $CH(g) \rightarrow C(g) + H(g)$	339
(5) $C(\text{graphite}) \rightarrow C(g)$	717
(6) $H_2(g) \rightarrow 2H(g)$	436

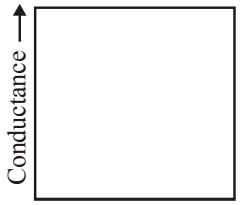
32. (a) (i) Draw the P-T phase diagram of water.
(ii) Label the different regions in this diagram.
(iii) On the diagram, show the liquid-vapour equilibrium for a dilute solution of NaCl, with the help of a dashed curve.

(b) The temperature dependence of the Gibb's free energy G is $\left(\frac{\partial\left(G/T\right)}{\partial T}\right)_P = \frac{H}{T^2}$

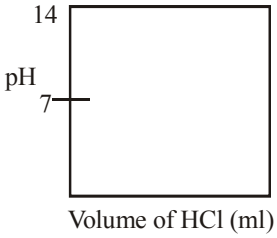
Obtain the expression for the temperature dependence of the equilibrium constant K given that $\Delta H^0 = A + BT$ (Where A and B are constants.)

33. (a) In the space provided, plot:

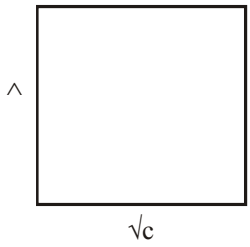
(i) Conductometric titration curve of 0.1 M $AgNO_3$ with 1 M NaCl, extended beyond the end point $\left(\lambda^0_{Na^+} \approx \lambda^0_{Ag^+}\right)$



(ii) pH vs. Volume of HCl, for a potentiometric titration of 0.1 (N) NH_4OH with 0.1 N HCl.



(iii) Variation of the molar conductivity of NaCl with the square root of its concentration.



(b) The $Zn^{2+} \mid Zn$ half cell $\left(E^\theta = -0.762\ V\right)$ is connected to a $Cu^{2+} \mid Cu$ halff cell $\left(E^\theta = 0.340\ V\right)$. What is the value of E^θ_{cell} for spontaneous conversion of chemical energy to electrical energy? What is the value of $\log_{10} K$, where K is the equilibrium constant? Use (2.303 RT/F) = 0.06.

34. (a) The following initial rate data were obtained for the reaction

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

	Partial Pressure of		Initial rate
	NO	O_2	
Run1	p_{NO}	p_{O_2}	v
Run 2	$2p_{NO}$	p_{O_2}	4v
Run 3	p_{NO}	$2p_{O_2}$	2v

(i) What is the rate law for this reaction?

(ii) One of the mechanisms proposed for this reaction is:

$$NO(g) + O_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3(g)$$

$$NO_3(g) + NO(g) \xrightarrow{k_2} 2NO_2(g)$$

Obtain the rate law predicted for this mechanism, assuming a stendy state concentration of NO_3.

(iii) Predict the rate law for this mechanism, if the first equilibrim step is established quickly and the second step is slow.

(b) (i) Write the expression for the vibrational contribution to the total energy of $CH_4(g)$ at 500 K. All the vibrational modes are active at this temperature.

(ii) Calculate the total internal energy of 1 mole of the gas at this temperature $R = 8.314\ J\ mol^{-1}K^{-1}$

35. (a) In the Bohr model of a hydrogen-like atom with atomic number Z,

- The angular momentum of an electron (of mass m_e and charge e) is a non-zero integral (n) multiple of $h/2\pi$, where h is the Plank's constant. and
- The electrostatic attraction exerted by the nucleus on the electron is balanced by the centrifula force experienced by the electron.

(i) Write mathematical expressions for the above statements.

(ii) Hence obtain the expression for the radius r of the Bohr orbit of the electron in terms of e, n, and Z.

(b) Complete the following nuclear reactions:

(i) $^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{1}_{1}H + ...$ (ii) $^{7}_{3}Li + ^{1}_{1}H \longrightarrow .....$

36. (a) Highly pure nicke metal can be prepared from its sulphide ore via $Ni(CO)_4$. Write the chemical equations involved.

(b) Addition of excess of aqueous NH_3 followed by ethanolic solution of dimethylglyoxime to a dilute aqueous solution of nickel sulphate changes the solution colour from green to blue to red. Write the strucures of the metal complexes corresponding to green, blue and red colours.

37. The element E on burning in the presence of O_2 gives F. Compound F on heating with carbon in an electric furnace gives G. On passing nitrogen over a heated mixture of F and carbon produces H. Steam can decompose H to produce boric acid and a colourless gas that gives white fumes with HCl. Identify F, G and H and give balanced equations for their formation.

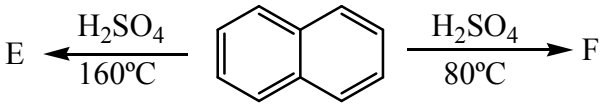
38. (a) Provide IUPAC names for the following complexes:

(i) $[CoCl(NH_3)_5]Cl_2$ (ii) $K_2[PdCl_4]$

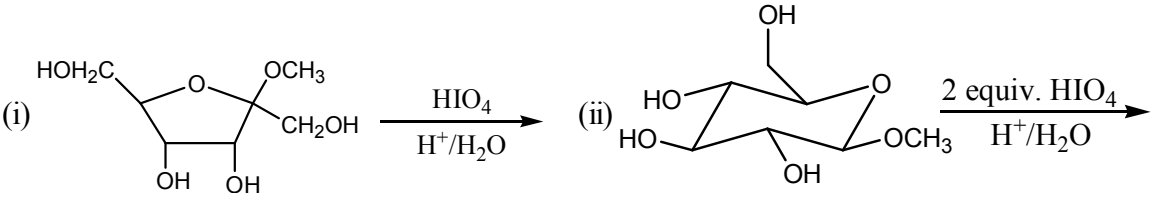
(b) The magnetic moment of $[Mn(H_2O)_6](NO_3)_2$ is approximately $6.0\ \mu_B$. Find the number of unpaired electrons, show crystal field splitting and calculate the CFSE.

39. A metal salt on heating with a mixture of KCl and conc. H_2SO_4 yields a deep red vapour J. The vapour on passing through an aqueous solution of KOH gives a yellow solution of compound K. Passing SO_2 gas through acidified solution (with H_2SO_4) of K leads to green colouration of the solution due to the formation of M. Identify J, K and M givingm balanced equations for the transformations, $J \rightarrow K$ and $K \rightarrow M$.

40. (a) Identify E and F in the following reactions and suggest a suitable reason for their formation.

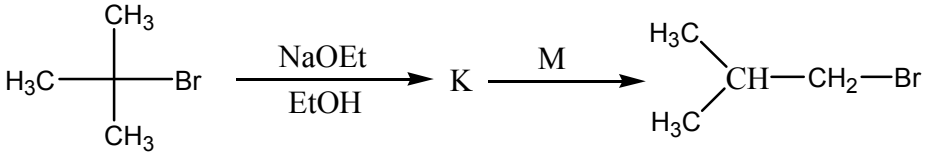


(b) Predict the products in each of the following reactions.

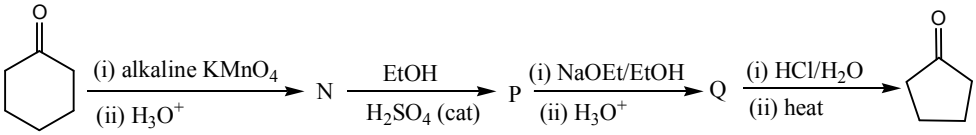


41. (a) A compound G having molecular formula C_6H_{12} decolourless both permagnanate and bromine water. G on ozonolysis followed by reductive work-up (Zn/H_3O^+) produces equal amounts of H and J with identical molecular C_3H_6O. Both H and J form 2, 4-dinitrophenyl hydrazones, however, only J shows positive test with Tollen's reagent. Identify the compounds G, H and J.

(b) Identify K and M in the following reaction sequence.

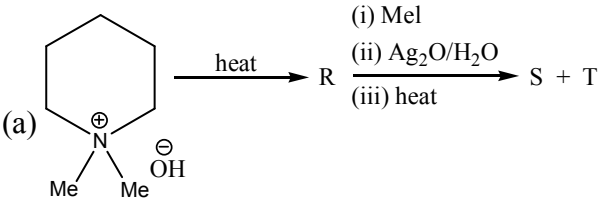


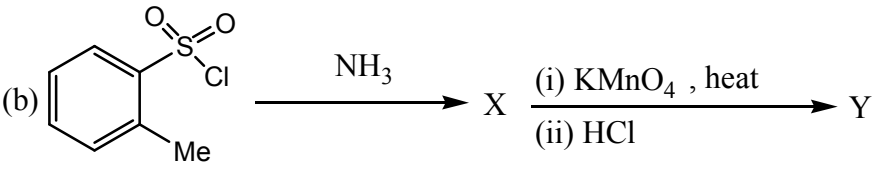
42. (a) Identify N, P and Q in the following synthetic transforamation.



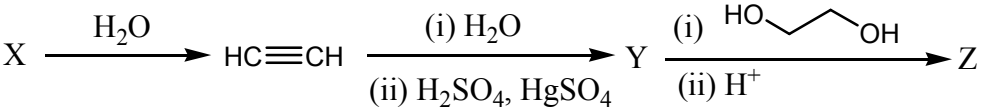
(b) Draw the most as well as the least stable chair conformations of trans-1-tert-butyl-4-methycyclohexane.

43. Identify R, S, T, X and Y in the following reaction sequences.





44. (a) Complete the following reaction sequence with the structures of X, Y and Z.



(b) Calculate the isoelectric point (pI) of lysine. Given the pK_a of $\alpha.NH_3$ is 8.95, pKa of side chain NH_3 is 10.53 and pK_a of $\alpha.COOH$ is 2.18.

IIT-JAM Chemistry Paper-2010

Instruction:
Q.1-30 (Objective questions) carry *three* marks each and Q.31-44 (Subjective questions) carry *fifteen* marks each.

1. The molar internal energy of a gas at temperature T is $U_m(T)$. The molar internal energy at T = 0 is $U_m(0)$. The correct expression that relates these two with appropriate contributions is:

(a) $U_m(T) = U_m(0) + 3RT$ [Linear molecule, translation only]

(b) $U_m(T) = U_m(0) + \frac{5}{2}RT$ [Linear molecule, translation and rotation only]

(c) $U_m(T) = U_m(0) + \frac{3}{2}RT$ [Nonlinear molecule, translation and rotation only]

(d) $U_m(T) = U_m(0) + RT$ [Non linear molecule, translation only]

2. If a particle has linear momentum $\vec{p} = -2\vec{i} + \vec{j} + \vec{k}$ at position $\vec{r} = 3\vec{i} - \vec{j} + \vec{k}$, then its angular momentum is:

(a) $\vec{i} + 2\vec{k}$ (b) $-2\hat{i} - 5\hat{j} + \hat{k}$ (c) $5\hat{i} - 2\hat{j}$ (d) $2\hat{i} + 5\hat{j} - \hat{k}$

3. If ψ is the eigenfunctions to hte Hamiltonian operator with α as the eigenvalue, then α MUST be
(a) Positive (b) Negative (c) An integer (d) Real

4. A quantum mechanical particle of mass m free to rotate on the surface of a sphere of radius r is in the state with energy $\frac{10\hbar^2}{mr^2}$. The degeneracy of this state is:
(a) 20 (b) 10 (c) 9 (d) 4

5. Choose the **INCORRECT** statement among the following:
(a) When ideal gases are mixed, the entropy of mixing is always positive.
(b) At equilibrium, the chemical potential of a species is the same in all of the phases of the system.
(c) The total pressure of a mixture of a ideal gases is equal to the sum of the partial pressure of each gas in the mixture
(d) When a gas is allowed to expand, the maximum work is obtained when the process is carried out irreversibly.

6. The work done during the free expansion of one mole of an ideal gas at 27ºC to twice its original volume is (given: RT = 2494 J mol^{-1}, ln 2 = 0.7, log 2 = 0.3)
(a) 1746 J mol^{-1} (b) –1746 J mol^{-1} (c) zero (d) 748.2 J mol^{-1}.

7. Choose the correct order of the diffusion coefficients of the following at 298 K.
P: H^+ in water Q: OH^- in water R: H_2O in water S: Sucrose in water
(a) P > Q > R > S (b) S > R > Q > P (c) S > Q > R > P (d) P > R > Q > S

8. Two matrices are given as $X = \begin{pmatrix} 1 & 5 \\ 3 & 7 \end{pmatrix}$ and $Y = \begin{pmatrix} 2 & 4 \\ 6 & 0 \end{pmatrix}$. If X^T is the transpose of X then what would be X^TY?

(a) $\begin{pmatrix} 20 & 52 \\ 4 & 20 \end{pmatrix}$ (b) $\begin{pmatrix} 20 & 4 \\ 52 & 20 \end{pmatrix}$ (c) $\begin{pmatrix} 32 & 4 \\ 48 & 12 \end{pmatrix}$ (d) $\begin{pmatrix} 44 & 28 \\ 12 & 12 \end{pmatrix}$

9. Addition of 1.0 g of a compound to 10 g of water increases the boiling point by 0.3ºC. The amount of compound needed to prepare a 500 ml of 0.1 M solution is (given: assume negligible dissociation or association of the compound, boiling point constant K_b of water = 0.513 kg mol^{-1})
(a) 0.855 g (b) 17.1 g (c) 8.55 g (d) 85.5 g

10. The molar conductivity of 0.009 M aqueous solution of a weak acid (HA) is 0.005 S m^2 mol^{-1} and the limiting molar conductivity of HA is 0.05 S m^2 mol^{-1} at 298 K. Assuming activity coefficients to be unity, the acid dissociation constant (K_a) of HA at this temperature is:
(a) 1×10^{-4} (b) 0.1 (c) 9×10^{-4} (d) 1.1×10^{-5}

11. The colour of potassium dichromate is due to
(a) d-d transition (b) transition in K^+ ion.
(c) Ligand to metal charge transfer (d) Metal-to-ligand charge transfer.

12. Which one of the following configuration will show Jahn-Teller distortion in an octahedral field?
(a) High spin d^8 (b) High spin d^4 (c) High spin d^5 (d) Low spin d^6.

13. B_2H_6 and B_4H_{10}, respectively, are examples of
(a) Nido and arachno borans (b) Nido and closo boranes
(c) Closo and arachno boranes (d) Nido boranes.

14. Which of the following has a square planar geometry according to the VSEPR theory? Atomic number: B = 5, S = 16, Xe = 54.
(a) XeO_2F_2 (b) SF4 (c) BF_4^- (d) XeF_4

15. The structure of rock salt consists of
(a) A cubic close-packed array of anions with cations in all the octahedral sites.
(b) A cubic close-packed array of cations with anions in all the tetrahedral sites.
(c) A hexagonal close-packed array of anions with cations in all the octahedral sites.
(d) A cubic close-packed array of anions with cations in all the tetrahedral sites.

16. Among lithium, nitrogen, carbon and oxygen, which element has the highest first ionization potential?
(a) Lithium (b) Nitrogen (c) Carbon (d) Oxygen

17. In which of the following C–H bond has the highest 's' character?
(a) Acetylene (b) Nitrogen (c) Carbon (d) Oxygen

18. Which one of the following is an electron deficient molecule according to the octet rule?
(a) CH_4 (b) $H_3N{:}BH_3$ (c) AlH_3 (d) GeH_4

19. Which one of the following has the highest lattice energy?
(a) LiCl (b) $CaCl_2$ (c) LiF (d) KCl

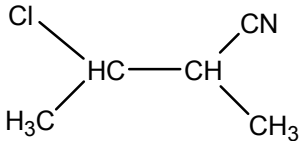
20. At room temperature, HCl is a gas while HF is a liquid because
(a) Of a strong bond between H and F in HF (b) HF is less acidic as compared to HCl
(c) Of strong intermolecular H-bonding in HF (d) HCl is less acidic as compared to HF

21. Benzene and Dewar benzene are

Benzene Dewar benzene

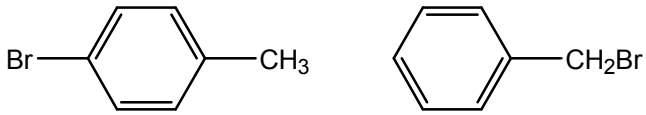
(a) Canonical forms (b) Structural isomers (c) Tautomers (d) Conformational isomers.

22. The IUPAC name of the following compound is:



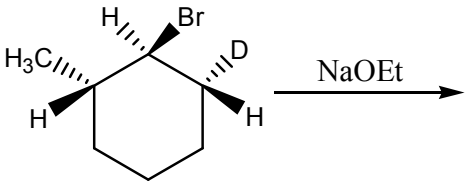
(a) 2-cyano-3-chlorobutane
(b) 2-chloro-3-cyanobutane
(c) 2-methyl-3-chlorobutanenitrile
(d) 3-chloro-2-methylbutanenitrile

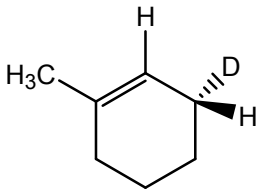
23. Which chemical test will distinguish the compounds shown below?

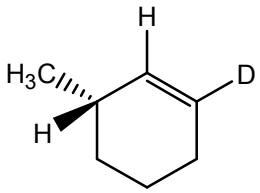


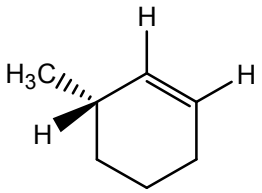
(a) Beilstein's flame test
(b) Ethanolic silver nitrate test
(c) Sodium fusion test
(d) Fehling's test

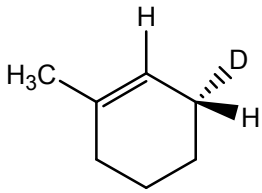
24. The reaction of the bromo compound shown below with sodium ethoxide gives predominantly

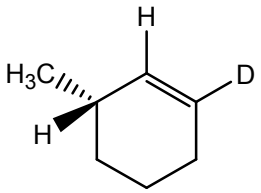


(a)


(b)


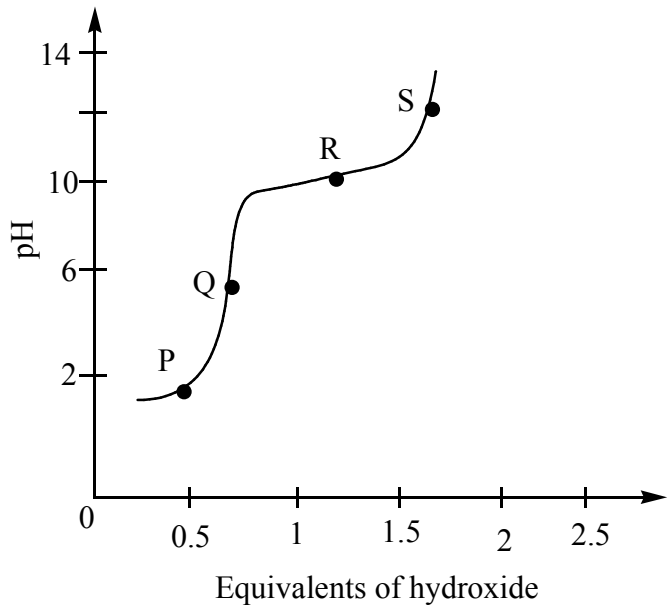
(c)


(d)


and


25. Choose the correct order of reactivity for dehydration of the given alcohols using concentrated sulfuric acid.
(a) 2-methylpropan-2-ol > 2-butanol > 1-butanol
(b) 2-methylpropan-2-ol > 1-butanol > 2-butanol
(c) 2-butanol > 2-methylpropan-2-ol > 1-butanol
(d) 1-butanol > 2-butanol > 2-methylpropan -2-ol.

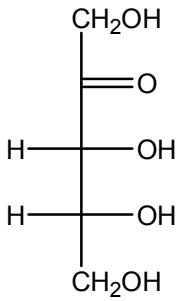
26. The titration curve of alanine hydrochloride is given below



The position in the graph that corresponds to the isoelectric point of alanine is:

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

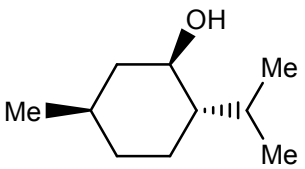
27. The absolute configurations at the two chiral centers in D-Ribulose are

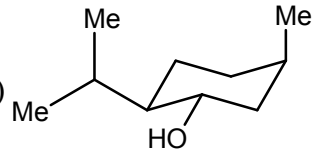


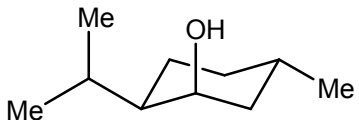
D-Ribulose

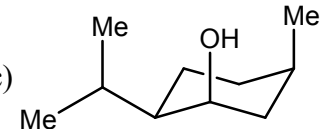
(a) 3R, 4R (b) 3R, 4S (c) 3S, 4R (d) 3S, 4S

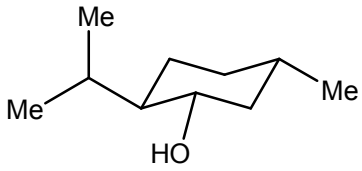
28. The most stable conformation of the molecule shown below is correctly represented by



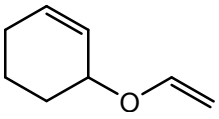
(a) 

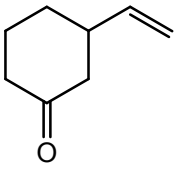
(b) 

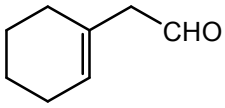
(c) 

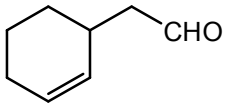
(d) 

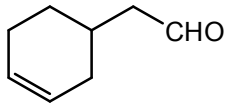
29. Thermal rearrangement of the following compound would give



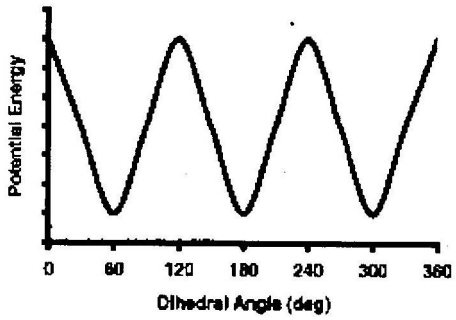
(a) 

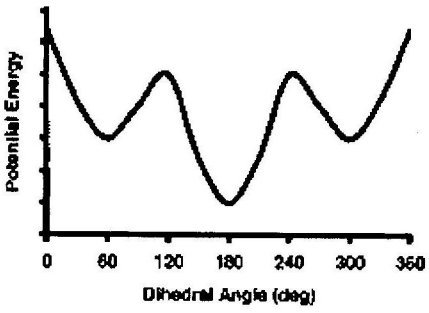
(b) 

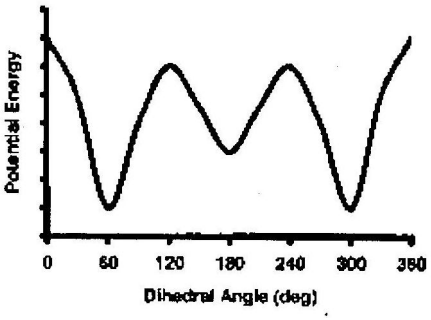
(c) 

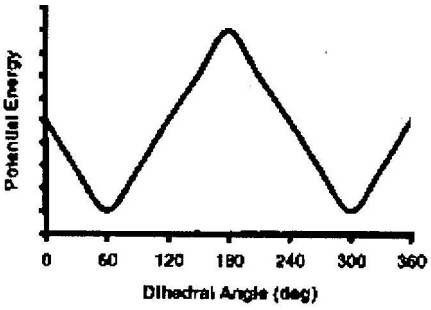
(d) 

30. The energy profile diagram that corresponds to 1, 2-dihydroxyethane for rotation around the C–C bond is

(a) 

(b) 

(c) 

(d) 

31. (a) Equilibrium constant for a reaction doubles as the temperature is increased from 300 K to 600 K. Calculate the standard reaction enthalpy (in kJ mol^{-1}) assuming it to be constant in this temperature range. (given R = 8.3 J K^{-1} mol^{-1}, ln = 2 = 0.7).

(b) A 50 mL solution of 0.1 M monoprotic acid ($K_a = 1\times10^{-5}$ at 298 K) is titrated with 0.1 M NaOH at 298 K. Calculate the solution after the addition of 50 mL of NaOH at this temperature. (given $Kw = 1\times10^{-14}$ at 298 K)

32. For the reaction

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

the following mechanism has been proposed.

Initiation:

$$Br_2 + M \xrightarrow{k_i} Br^{\bullet} + Br^{\bullet} + M$$

Propagation:

$$Br^{\bullet} + H_2 + \xrightarrow{k_p} HBr + H^{\bullet}$$

$$H^{\bullet} + Br_2 \xrightarrow{k_{p'}} HBr + Br^{\bullet}$$

Retardation:

$$H^{\bullet} + HBr \xrightarrow{k_r} H_2 + Br^{\bullet}$$

Termination:

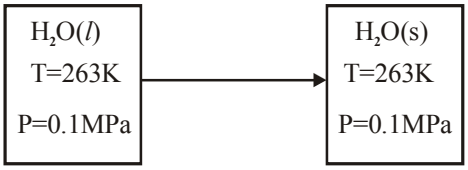
$$Br^{\bullet} + Br^{\bullet} + M \xrightarrow{k_t} Br_2 + M + \text{energy}$$

Where M is the initiator/terminator.

(a) Write the differential rate equations for the formation of the two intermediates $H^{\bullet}$ and $Br^{\bullet}$.

(b) Using the steady-state approximate calculate the concentration of the intermediate $H^{\bullet}$ and $Br^{\bullet}$ and obtain the rate law for the formation of HBr.

33. Calculate ΔH_m and ΔS_m for the process



Assume that at 273 K the molar enthalpy of fusion of ice is 6006 J mol^{-1}, the heat capacity $C_{p,m}(s)$ of ice is 38 J K^{-1} mol^{-1} and heat capacity $C_{p,m}(\ell)$ of liquid water is 76 J K^{-1} mol^{-1}. Consider the heat capacities to be constants. Consider the heat capacities to be constants.
(given: ln = 263 = 5.57 and ln 273 = 5.61)

34. Two beakers, one containing 0.02 M $KMnO_4$, 0.2 M $MnSO_4$ and 0.5 M H_2SO_4 and another containing 0.15 M $FeSO_4$ and 0.05 M $Fe_2(SO_4)_3$, are connected by a salt-bridge Platinum electrodes are placed in each beaker and these two electrodes are connected via a wire with a voltmeter in between. H_2SO_4 is present in equal volumes in each beaker. Assume H_2SO_4 is completely ionized.

Given: $E^0_{Fe^{3+}/Fe^{2+}} = 0.8V$, $E^0_{MnO_4^-/Mn^{2+}} = 1.5$ V, $\frac{2.303RT}{F} = 0.06V$ and log2=0.3

(a) Write the complete balanced redox reaction for this cell.
(b) What would be the potential of each half-cell after the reaction has reached equilibrium?

35. An atomic orbital is described by the wavefunction

$$\psi(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\left(\frac{r}{a_0}\right)}, \text{ where } a_0 \text{ is the Bohr radius.}$$

Given: $d\tau = r^2 \sin\theta dr d\theta d\phi$ and $\int_0^{\infty} r^n e^{-\beta r} d\tau = \frac{n!}{\beta^{n+1}}$ (n is a positive integer)

(a) Identify the atomic orbital and calculate the mean or the average radius of this orbital in terms of a_0.
(b) Calculate the most probable radius (in terms of a_0) at which an electron will be found when it occupies this orbital.

36. Identify W, X, Y and Z in the following sequence.

$$Li + W(g) \xrightarrow{\text{heat}} \underset{(\text{read})}{X} \xrightarrow{H_2O} Y(g) \xrightarrow{\text{alkaline } K_2HgI_4} \underset{(\text{brown})}{Z}$$

Y turns moist litmus paper blue. Write balanced chemical equation for the conversion of Y to Z.

37. (a) Draw the crystal field splitting diagram with appropriate labels for $[NiCl_4]^{2-}$. Determine the spin only magnetic moment and the crystal field stabilization energy (CFSE) for this complex. (given: atomic number of Ni = 28)

(b) Write the balanced equations for the reactions involved in the iodometric estimation of Cu^{2+} using thiosulfate.

38. (a) In the reaction sequence given below P is an anionic Fe(II) complex.

$$P \xrightarrow{aq.NO_2^-} \underset{(brown)}{Q} \xrightarrow{aq.S^{2-}} \underset{(purple)}{R}$$

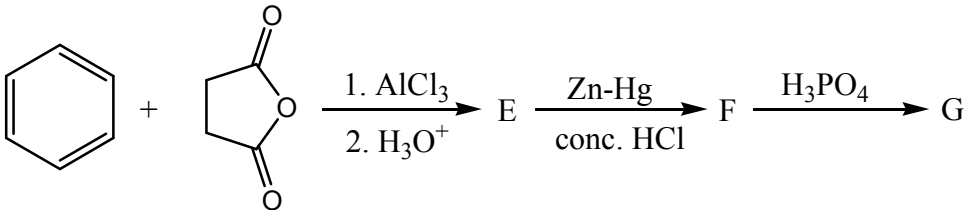
Identify P, Q and R.

(b) Draw a properly labeled unit cell diagram of CsCl. Show through calculations that there is only one CsCl per unit cell.

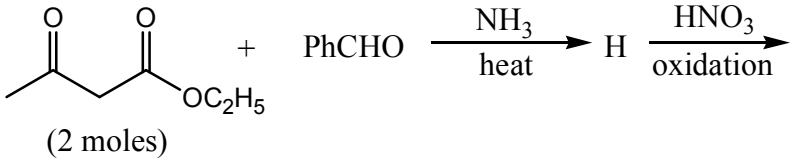
39. (a) Write the balanced chemical equations for the reactions involved in the synthesis of borazine using ammonium chloride as one of the starting materials. Write the structure of borazine.

(b) Draw Lewis structures of SF_4 and NO_3^-

40. (a) Complete the following sequence by identifying E, F and G.

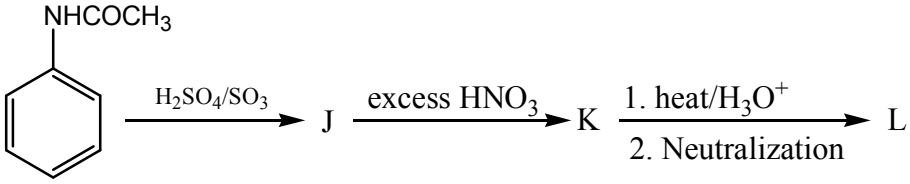


(b) Identify H and I in the reactions below

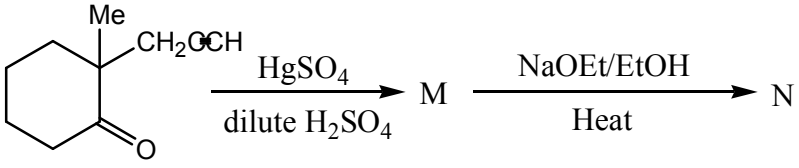


(2 moles)

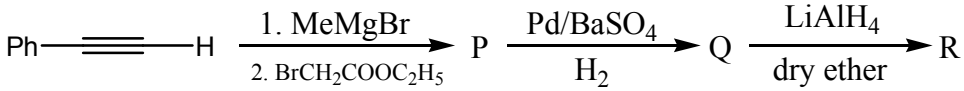
41. (a) Identify the products J, K, and L in the following reactions. Lassigne's test for L shows the presence of nitrogen only.



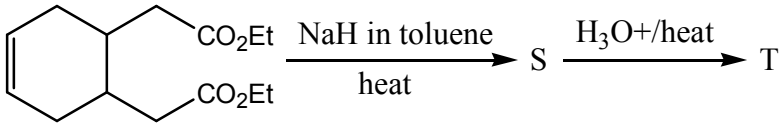
(b) Write the structure of M and N in the following reactions.



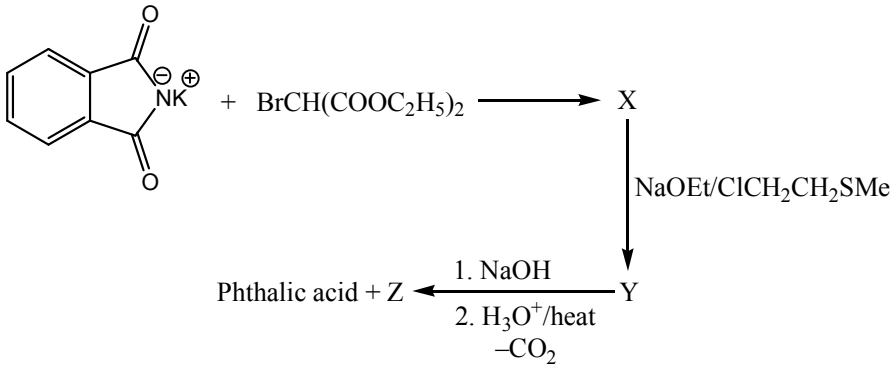
42. (a) Write the structures of P, Q and R in the given reaction sequence.



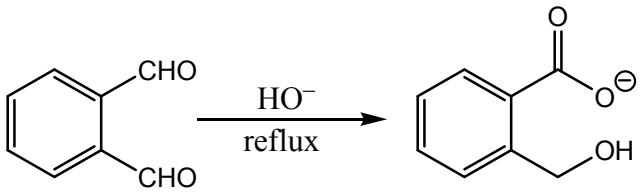
(b) Identify S and T in the reactions given below:



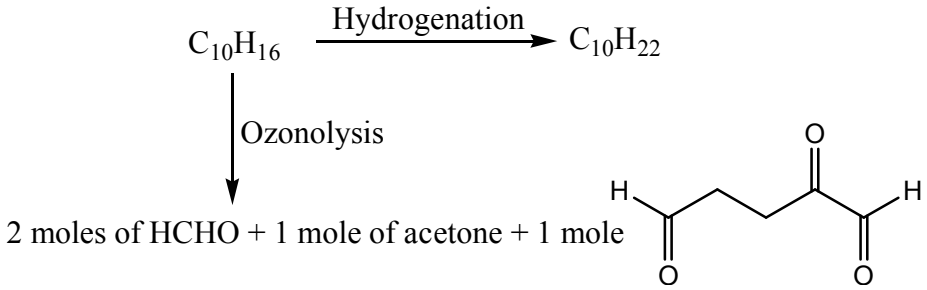
43. (a) Identify X, Y and Z in the following reactions.



(b) Suggest a suitable mechanism for the following reaction.



44. Consider the following reactions for a compound with molecular formula $C_{10}H_{16}$.



(a) Write structues that are consistent with the above data for the formula $C_{10}H_{16}$.

(b) Given that myrcene is a terpene and has the molecular formula $C_{10}H_{16}$, using the isoprene rule identify the correct structure for myrcene among the structures elucidated in part(a).

IIT-JAM Chemistry Paper-2011

Instruction:
Q.1-30 (Objective questions) carry *three* marks each and Q.31-44 (Subjective questions) carry *fifteen* marks each.

1. The pair of semimetals in the following is:
(a) Al, Si (b) Ge, As (c) Sb, Te (d) Ca, B

2. The most probable oxidation states for both Cr and Mo are
(a) +2, +3, +4 (b) +2, +3, +5 (c) +2, +3, +6 (d) +3, +4, +5

3. The correct order of acidic character is:
(a) $Al_2O_3 > MgO > SiO_2 > P_4O_{10}$ (b) $P_4O_{10} > Al_2O_3 > MgO > SiO_2$
(c) $P_4O_{10} > SiO_2 > Al_2O_3 > MgO$ (d) $SiO_2 > P_4O_{10} > Al_2O_3 > MgO$

4. The pair of amphoteric oxides is:
(a) VO, Cr_2O_3 (b) V_2O_3, Cr_2O_3 (c) VO_2, Cr_2O_3 (d) V_2O_5, CrO_3

5. In the structure of $B_4O_5(OH)_4^{2-}$
(a) All four B atoms are trigonal planar
(b) One B atom is tetrahedral and the other three are trigonal planar.
(c) Three B atoms are tetrahedral and one is trigonal planar.
(d) Two B atoms are tetrahedral and the other two are trigonal planar.

6. The pH of an aqueous solution of Al^{3+} is likely to be
(a) Neutral (b) Acidic (c) Slightly basic (d) Highly basic.

7. Hydrolysis of $(CH_3)_2SiCl_2$ and CH_3SiCl_3 leads to
(a) Linear chain and cross-linkedsilicones, respectively
(b) Cross-linked and linear chain silicones, respectively.
(c) Linear chain silicones only
(d) Cross-linked silicones only.

8. The oxide that has the inverse spinel strucrure is:
(a) $FeCr_2O_4$ (b) $MnCr_2O_4$ (c) $CoAl_2O_4$ (d) Fe_2CoO_4

9. The transition metal monoxide that shows metallic conductivity is:
(a) NiO (b) MnO (c) TiO (d) CoO

10. The metal that is extracted by the reduction method is:
(a) Al (b) Au (c) Hg (d) Mg

11. The most viscous liquid is:
(a) Water (b) Methanol (c) Ethylene glycol (d) Glycerol

12. In ammonical buffer, oxine (8-hydroxyquinoline) forms yellow precipitate with
(a) Mg(II) (b) Ca (II) (c) Ba (II) (d) Sr (II)

13. Addition of an aqueous solution of Fe(II) to potassium hexacyanochromate (III) produces a brick-red coloured complex, which turns dark green at 100 °C. The dark green complex is:
(a) $Fe_4[Cr(CN)_6]_3$ (b) $KFe[Cr(CN)_6]$ (c) $KCr[Fe(CN)_6]$ (d) $Fe[Cr(CN)_6]$

14. In the following equation X is $^{241}_{95}Am + \alpha \longrightarrow {}^{243}_{97}Bk + X$

(a) $2\,{}^{1}_{0}n$ (b) ${}^{1}_{0}n$ (c) $2\,{}^{1}_{1}n$ (d) ${}^{4}_{2}He$

15. Based on the principle of equipartition of energy, the molar heat capacity of CO_2 at constant volume $C_{v,m}$ is:
(a) 3.5 R (b) 6R (c) 6.5R (d) 9R

16. One mole of a van der waals gas undergoes reversible isothermal transformation from an initial volume V_1 to a final volume V_2. The expression for the work done is:

(a) $RT\ln\frac{V_2}{V_1} + a\left(V_2 - V_1\right)$ (b) $-RT\ln\frac{V_2 - b}{V_1 - a} + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

(c) $RT\ln\frac{P_2}{P_1}$ (d) $RT\ln\frac{V_2 - b}{V_1 - a} - a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

17. The scalar product of two vectors u and v, where $u = 2\hat{i} + 3\hat{j} - 5\hat{k}$ and $v = \hat{i} + \hat{j} + 3\hat{k}$, is:

(a) -10 (b) $2\hat{i} + 3\hat{j} - 15\hat{k}$ (c) $3\hat{i} + 4\hat{j} - 2\hat{k}$ (d) 10

18. The minimum concentration of silver ions that is required that is required to start the precipitation of Ag_2S ($K_{sp} = 1\times10^{-51}$) in a 0.1 M solution of S^{2-} is:
(a) 1×10^{-49} M (b) 1×10^{-50} M (c) 1×10^{-26} M (d) 1×10^{-25} M

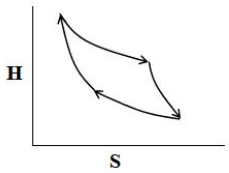
19. Identify the correct statement regarding Einsteins's photoelectric effect
(a) The numbr of electrons ejected depends on the wavelength of incident radiation.
(b) Electron ejection can occur at any wavelength of incident radiation.
(c) The number of electrons ejected at a given incident wavelength depends on the intensity of the radition.
(d) The kinetic energy of the ejected electrons is independent of the wavelength of incident radiation.

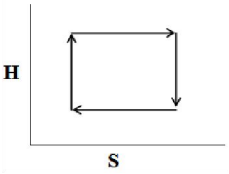
20. The hydrolysis constant (K_h) of NH_4Cl is 5.6×10^{-10}. The concentration of H_3O^+ in a 0.1 M solution of NH_4Cl at equilibrium is:

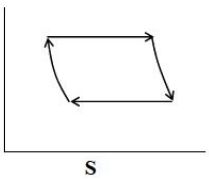
(a) $\sqrt{5.6\times10^{-11}}$ (b) $\sqrt{5.6\times10^{-10}}$ (c) 5.6×10^{-10} (d) 2.8×10^{-5}

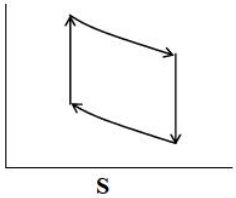
21. The acid dissociation constant (K_a) for HCOOH, CH_3COOH, $CH_2ClCOOH$ and HCN at 25ºC are $1.8\times10^{-4}, 1.8\times10^{-5}, 1.4\times10^{-3}$ and 4.8×10^{-10}, respectively. The acid that gives highest pH at the equivalence point when 0.2 M solution of each acid is titrated with a 0.2 M solution of sodium hydroxide is:
(a) HCOOH (b) CH_3COOH (c) $CH_3ClCOOH$ (d) HCN.

22. For an ideal gas undergoing reversible Carnot Cycle, the plot of enthalpy (H) versus entropy (S) is:

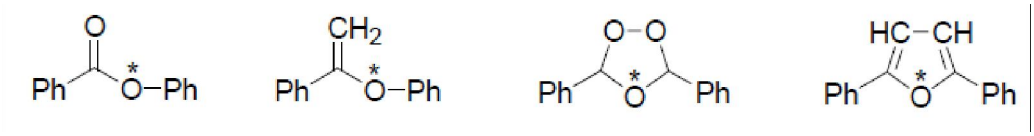
(a) 

(b) 

(c) 

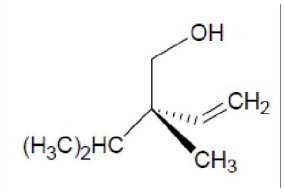
(d) 

23. Hybridizations of the atoms indicated with the asterisk (*) in the following compounds sequantly are



(a) sp^2, sp^2, sp^3, sp^2 (b) sp^2, sp^3, sp^3, sp^2 (c) sp^3, sp^3, sp^3, sp^2 (d) sp^2, sp^2, sp^3, sp^3

24. The Cahn-Ingold-Prelog (CIP) priorities of the groups and the absolute configuration (R/S) of the following comopund are



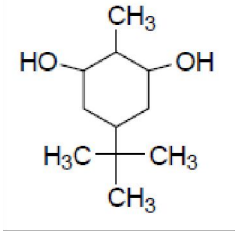
(a) $CH_2OH > CH(CH_3)_2 > CH = CH_2 > CH_3$ and S

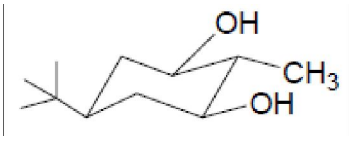
(b) $CH_2OH > CH = CH_2 > CH(CH_3)_2 > CH_3$ and S

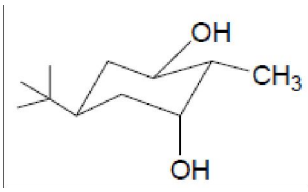
(c) $CH_2OH > CH = CH_2 > CH(CH_3)_2 > CH_3$ and R

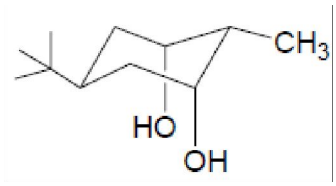
(d) $CH_2OH > CH(CH_3)_2 > CH = CH_2 > CH_3$ and R

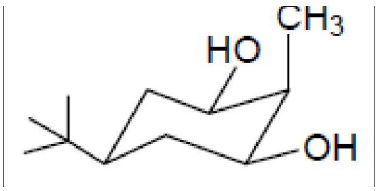
25. The optically active stereoisomer of the following compound is:



(a) 

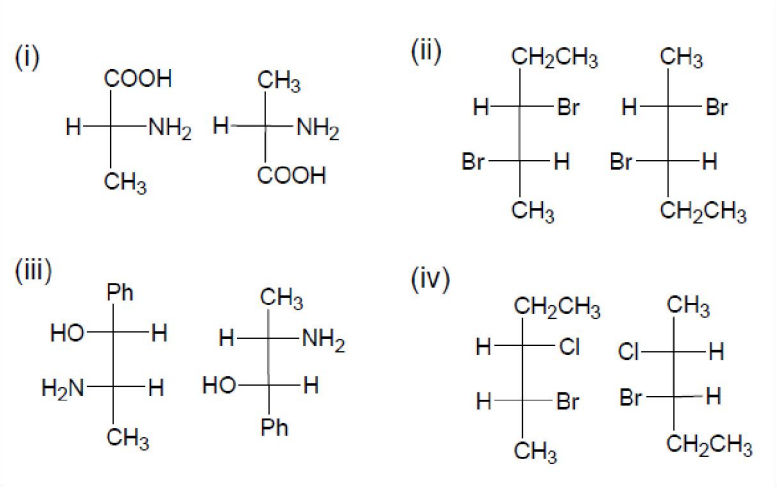
(b) 

(c) 

(d) 

26. The correct relationship within each pair of the natural products is:
(a) Camphor – terpene; insulin – protein; nicotine – alkaloids; streptomycin – carbohydrate
(b) Camphor – terpene; insulin – carbohydrate; nicotine – alkaloid; streptomycin – lipid
(c) Camphor – alkaloid; insulin – protein; nicotine – terpene; streptomycin – carbohydrate.
(d) Camphor – carbohydrate; insulin – protein; nicotine – alkaloid; streptomycin –terpene.

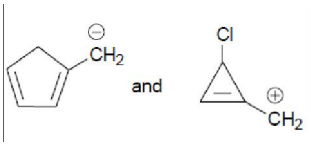
27. The correct sequence of relationships between the compounds of the following pairs i-iv is:

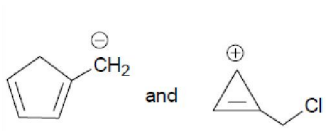


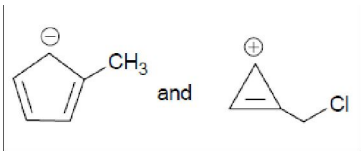
(a) Identical, enantiomers, diastereomers and structural isomers.
(b) Enantiomers, identical, structural isomers and disastereomers.
(c) Enantiomers, identical, diasteromers and structural isomers.
(d) Identical, identical, diastereomers and structural isomers.

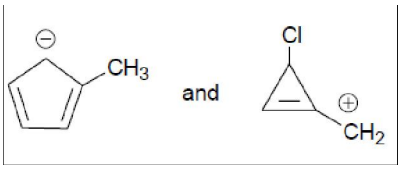
28. The INCORRECT statement in the following is:
(a) The nucleobase pairs are aligned perpendicular to the helical axis in DNA.
(b) RNA contains uracil and thymine, but DNA contains only thymine.
(c) All naturally occuring amino acids with the exception of glycine are chiral
(d) All enzymes are proteins, but all proteins are not necessarily enzymes.

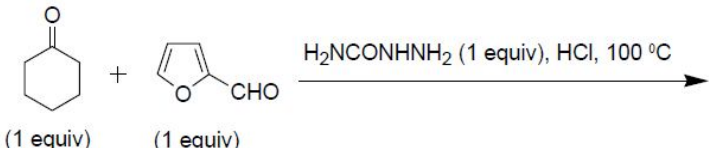
29. The product P and Q in the following reactions, respectively, are

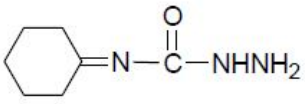
(a) 

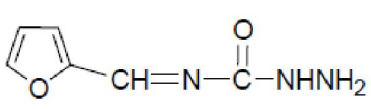
(b) 

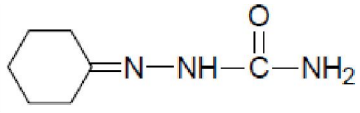
(c) 

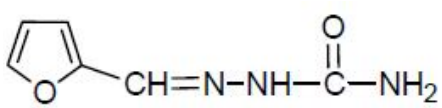
(d) 

30. The major product in the following reaction is 

(a) 

(b) 

(c) 

(d) 

31. (a) In the following reactions, identify X, Y and Z.

$$Na_2SO_3 + S \xrightarrow{\text{boiling water}} \mathbf{X} \text{ (colorless solid)}$$

$$AgBr \xrightarrow{\text{excess } \mathbf{X}} \mathbf{Y} \text{ (soluble complex)}$$

$$\mathbf{X} + Cl_2 + H_2O \xrightarrow{\text{boiling water}} \mathbf{Z} + HCl$$

(b) Draw the structures of $S_4N_4H_4$ and $N_4S_4F_4$.

32. (a) The magnetic moment of $\left[Fe(phen)_2(NCS)_2\right]$ varies with temperature. The magnetic moments at 200 K and 50 K are 4.9 BM and 0 BM, respectively. Write the d-electron configurations of Fe at both temperatures and give reason for the observed change in the magnetic moment.
(phen = 1, 10-phenanthroline)

(b) PCl_5 exists as a discrete convalent molecule in the gaseous state, but is ionic in the solid state. Draw the structures of PCl_5 in gaseous and solid states.

33. In the following equilibrium and reactions, identify species B to E.
Write the balanced chemical equation for the conversion of C to E.

$$\mathbf{A} \xrightarrow{pH > 6} \mathbf{B} \underset{}{\overset{\text{dil. HCl}}{\rightleftharpoons}} \mathbf{C}$$

- **A**: oxide of Cr; solid; no *d*-electrons
- **B**: yellow color; tetrahedral
- **C**: strong oxidizing agent

$$\mathbf{B} + \text{diphenylcarbazide} \longrightarrow \mathbf{D} \text{ (violet color)}$$

$$\mathbf{C} + HCl \longrightarrow \mathbf{E} \text{ (greenish yellow gas)}$$

34. (a) Identify species A and C in the following.
Write the balanced chemical equation for the conversion of A to A^{3+}.

$$\mathbf{A} + \text{aquaregia} \longrightarrow \mathbf{A}^{3+} + NO$$

$$\mathbf{A}^{3+} + I^- \longrightarrow \mathbf{B} \text{ (black precipitate)}$$

$$\mathbf{B} + I^- \text{(excess)} \rightleftharpoons \mathbf{C} \text{ (orange color)}$$

Hint: C on the dilution with water gives B

(b) Draw the structures of X and Y in the following reactions.

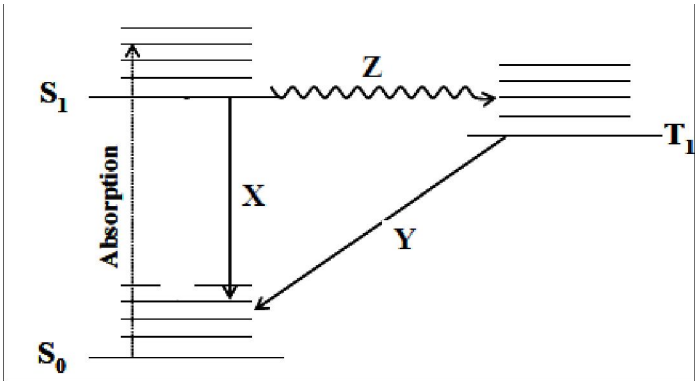
(i) Borazine + $HCl \longrightarrow$ **X**

(ii) Borazine + $Br_2 \longrightarrow$ **Y**

35. (a) The molar conductances at infinite dilution for $BaCl_2$, KCl, K_2SO_4 and Cl^- are 280, 150, 300 and 76 $\Omega^{-1}m^2mol^{-1}$, respectively. Calculate the transport number of Ba^{2+} in $BaSO_4$ solution at infinite dilution.

(b) If 4 moles of a MX_2 salt in 1 kg of water raises the boiling point of water by 3.2 K. Calculate the degree of dissociation of MX_2 in the solution.

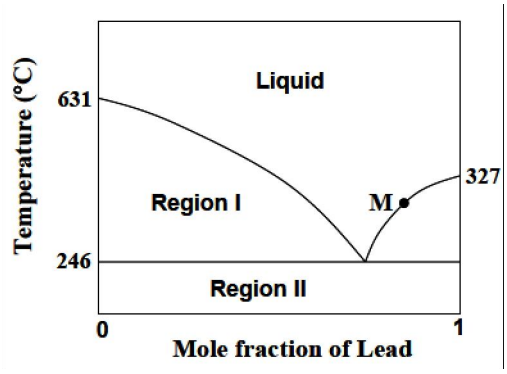
36. (a) For the reaction $R \rightarrow P$, the plot of ln[R] versus time (t) gives a straight line with a negative slope. The half life for the reaction is 3 minutes.
(ln 2 = 0.693, ln 0.1 = – 2.303)
(i) Derivative the expression for $t_{1/2}$.
(ii) Calculate the slope of the straight line
(iii) Calculate the time required for the concentration of R to decrease to 10% of its initla value.
(b) Shown below is the Jablonski diagram that that describes various photophysical processes. The solid arrows represent radiative transitions and the wavy arrow represents a non-radiative transition.



(i) Name the photophysical pathways X, Y and Z.
(ii) Which of the radiative decays in faster?

37. (a) (i) Given that $\Delta G = -nFE$, derive the expression for the temperature dependence of the cell potential (E) in terms of the change in entropy (ΔS).

(ii) For a cell reaction, E(at 25ºC) = 1.26 V, n =2 and $\Delta S = -96.5\ J\ K^{-1}mol^{-1}$. Calculate E at 85º C by assuming ΔS to be independent of temperature. ($F = 965000\ C\ mol^{-1}$).
(b) The phase diagram for the lead-antimony system at a certain pressure is given below.



(i) Identify the phases and components in region I and region II.
(ii) Calculate the number of degrees of freedom (Variance) at point M.

38. (a) One mole of an ideal gas initially at 300 K and at a pressure of 10 atm undergoes adiabatic expansion.
(i) Reversibly and
(ii) Irreversibly against a constant external pressure of 2 atm until the final pressure becomes equal to the external pressure.

Calculate ΔS_{system} for (i) and (ii). For (ii), express the final answer in terms of R. Given: Molar heat capacity at constant volume $C_{v,m} = 3R/2$.

(b) For the following equilibrium at 300 °C.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Calculate K_p when N_2O_2 is 30% dissociated and the total pressure is 2 bar.

39. (a) The Maxwell probability distribution of molecular speeds for a gas is:

$$F(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv$$

where 'v' is the speed, 'm' the mass of a gas molecule and k teh Boltzmann constant.
(i) Use F(v) to show that the most probable speed v_{mp} is given by the expression.

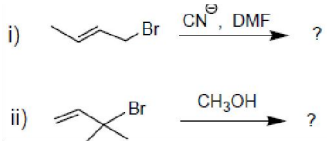
$$v_{mp} = \left(\frac{2RT}{M}\right)^{1/2}$$

(ii) Use R = 8 J K^{-1} mol^{-1} in the above expression to calculate the v_{mp} for $CH_4(g)$ at 127 °C.
(b) The wavefunction of a quantum state of hydrogen atom with principal quantum number n = 2 is:

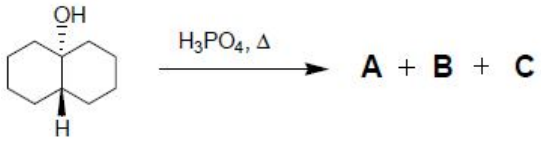
$$\psi_{2\ell m}(r,\theta,\phi) = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right)$$

(i) Identify the values of quantum numbers *l* and m and hence the atomic orbital.
(ii) Find where the radial node of the wavefunction occurs.

40. (a) Write the possible substitution products in the following reactions. Indicate the types of mechanisms (S_N1/ S_N2/S_N2) that is/are operative in each reaction.

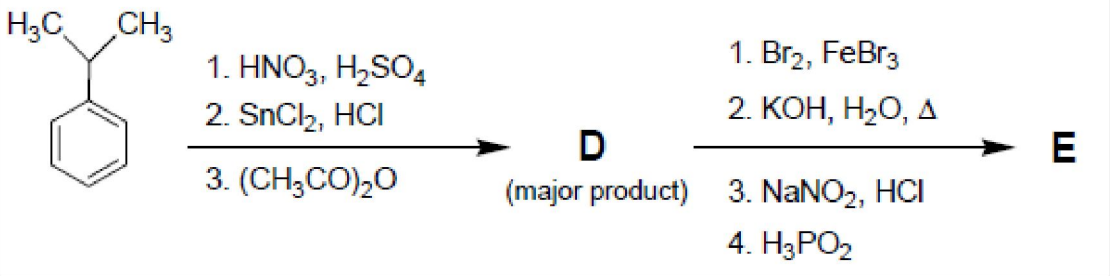


(b) Write the elimination products A to C in the following reaction. Identify the major product

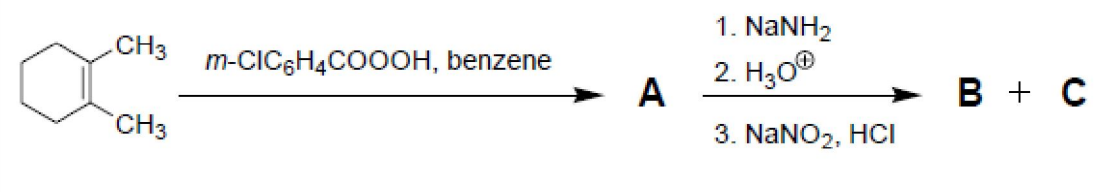


41. (a) Write the structures of A to C in the following reaction sequence.

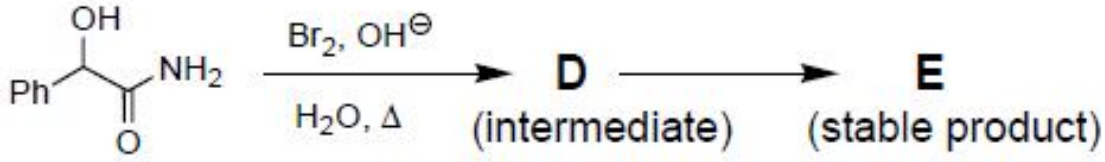
(b) Write the structures of D and E in the reactions given below.



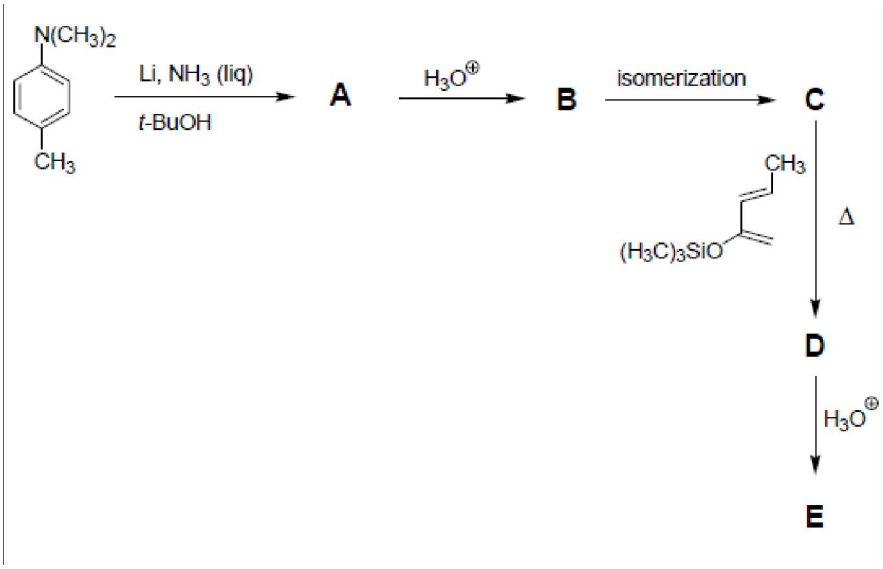
42. (a) Write the structures of A to C in the following reaction sequence.



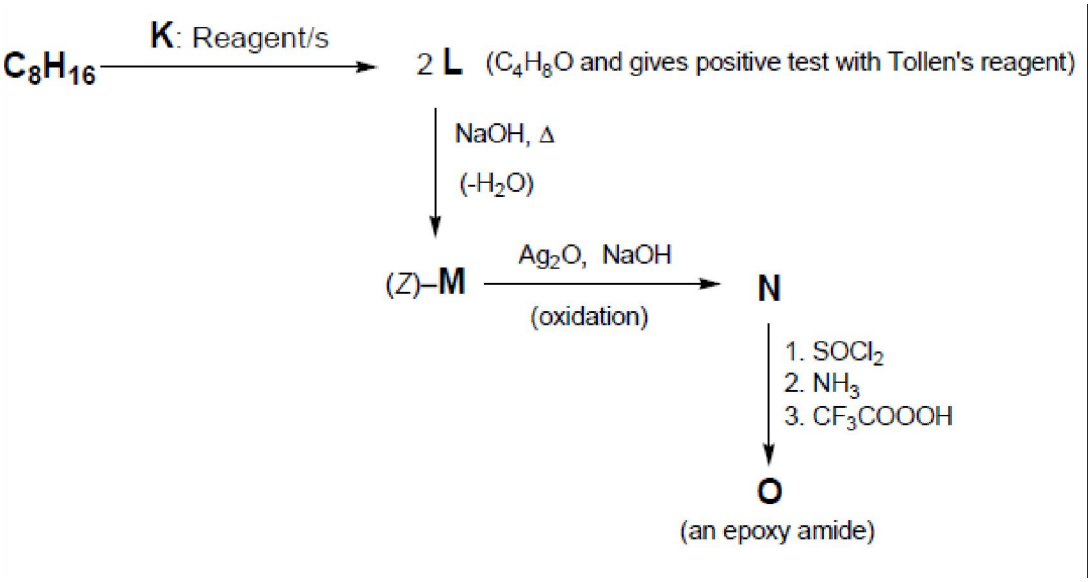
(b) Write the structures of D and E in the following reaction.



43. Write the structures of products A to E in the following reaction sequence.



44. Oxanamide O, a tranquilizer, is synthesized according to the following reaction scheme. Write the missing structures and reagents K to O.



IIT-JAM Chemistry Paper-2012

Instruction:
Q.1-30 (Objective questions) carry *three* marks each and Q.31-44 (Subjective questions) carry *fifteen* marks each.

1. Molecular shape of $SOCl_2$ is:
(a) Square planar (b) Trigonal pyramidal (c) Triangular planar (d) T-shape

2. Number of three-centre two-electron(3c-2e) bonds present in diborane is:
(a) 2 (b) 4 (c) 6 (d) 8

3. The lattice energy of LiF calculated from Born-Lande equation –1000 kJ mol^{-1}. Assume that for both LiF and MgO the Madelung constants, interionic distances and Born exponents have the same value. The lattice energy of MgO in kJ mol^{-1} is:
(a) –4000 (b) –2000 (c) 2000 (d) 4000

4. The compound formed by dissolving elemental gold in *aqua regia* is:
(a) AuCl (b) $AuNO_3$ (c) $H[AuCl_4]$ (d) $H[Au(NO_3)_4]$

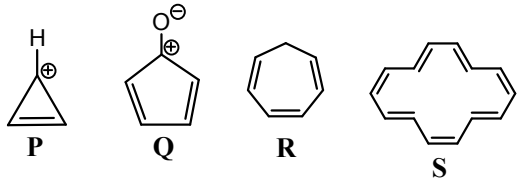
5. Number of moles of ions produced by complete dissociation of one mole of Mohr's salt in water is:
(a) 3 (b) 4 (c) 5 (d) 6

6. The tetrachloro complexes of Ni(II) and Pd(II) respectively, are (atomic numbers of Ni and Pd are 28 and 46 respectively)
(a) diamagnetic and diamagnetic (b) paramagnetic and paramagnetic
(c) diamagnetic and paramagnetic (d) paramagnetic and diamagnetic

7. The total number of steps involved and number of beta particles emitted in the spontaneous decay of $^{238}_{92}U \rightarrow {}^{208}_{82}Pb$ respectively, are
(a) 8 and 6 (b) 14 and 6 (c) 6 and 8 (d) 14 and 8

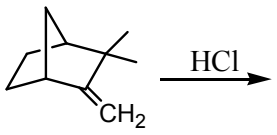
8. A filter paper moistened with ammonical sodium nitroprusside solution turns violet on contact with a drop of alkaline Na_2S solution. The violet color is due to the formation of
(a) $\left[Fe(SCN)_5(NO)\right]^{1-}$ (b) $\left[Fe(SCN)_5(NO)\right]^{2-}$ (c) $\left[Fe(CN)_5(NOS)\right]^{3-}$ (d) $\left[Fe(CN)_5(NOS)\right]^{4-}$

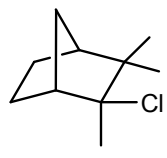
9. The species/compounds that are aromatic among the following are

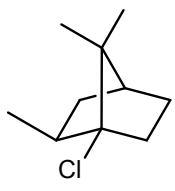


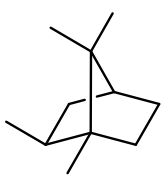
(a) R and S (b) P and Q (c) Q and S (d) P and S

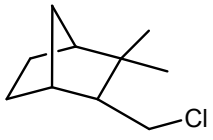
10. The major product obtained in the reaction below is



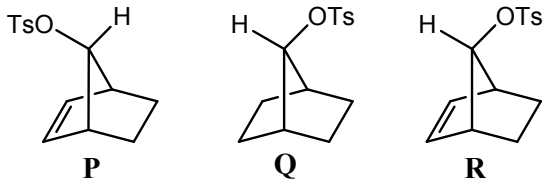
(a) 

(b) 

(c) 

(d) 

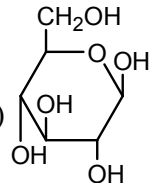
11. The rates of acetolysis for the following norbornyl derivatives are in the order

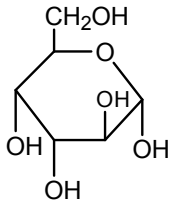


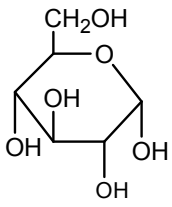
P **Q** **R**

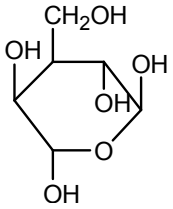
(a) R > Q > P (b) Q > R > P (c) P > R > Q (d) R > P > Q

12. The Haworth projection for α – anomer of D-glucose is:

(a) 

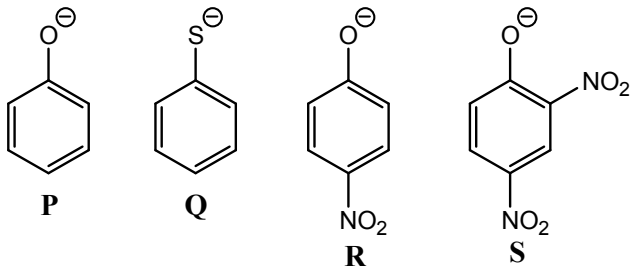
(b) 

(c) 

(d) 

13. The complementary DNA sequence of the given DNA 5'-G-A-A-T-T-C-3' is:
(a) 5'-C-T-T-A-A-G-3' (b) 5'-C-U-U-A-A-G-3'
(c) 3'-C-T-T-A-A-G-5' (d) 3'-G-A-A-T-T-C-5'

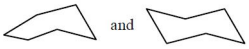
14. The order of nucleophilicity of the following anions in a S_N2 reaction is:

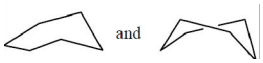


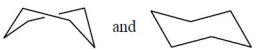
P **Q** **R** **S**

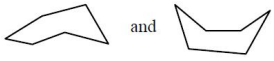
(a) Q > R > S > P (b) Q > P > R > S (c) Q > R > P > S (d) P > S > R > Q

15. The pair of conformation that has maximum energy difference is:

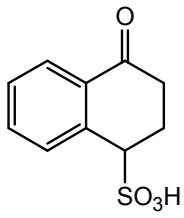
(a) 

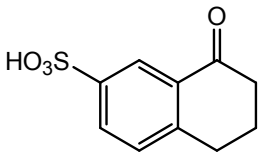
(b) 

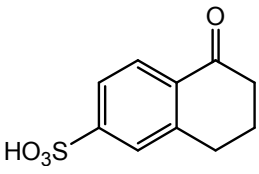
(c) 

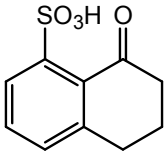
(d) 

16. The major mono-sulfonation product of α – tetralone is :

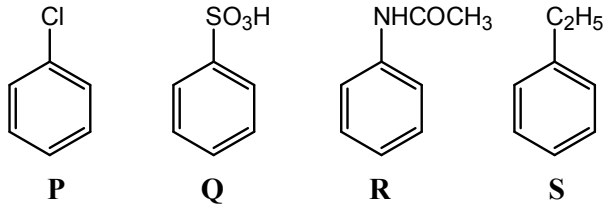
(a) 

(b) 

(c) 

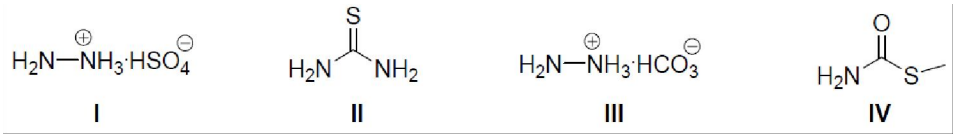
(d) 

17. Electrophilic nitrations of the following compounds follow the trend



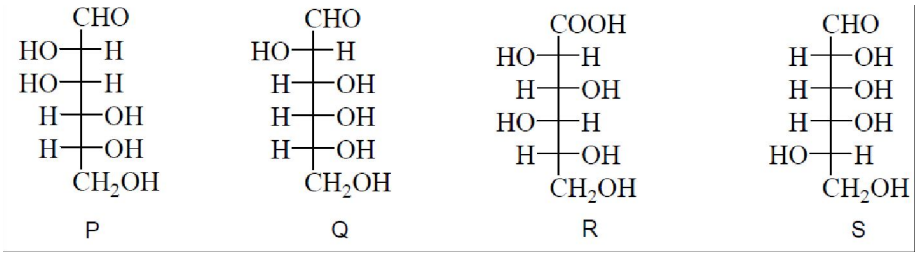
(a) S > R > P > Q (b) R > S > P > Q (c) R > P > S > Q (d) P > S > R > Q

18. The compounds those would not respond to tests of both nitrogen and sulfur with sodium fusion extracts are



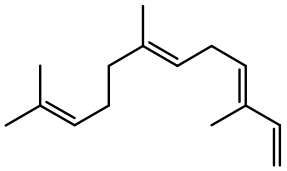
(a) I and III (b) III and IV (c) I and IV (d) II and IV

19. The correct epimeric pair of the following is:



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

20. α – Farnesene shown below is a



(a) diterpene having two isoprene units (b) triterpene having three isoprene units
(c) triterpene having four isoprene units (d) sesquiterpene having three isoprene units.

21. For the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the equilibrium constant, K_p is expressed as

(a) $3^2 K_p = \frac{p_{NH_3}}{p_{N_2}^2}$ (b) $3^2 K_p = \frac{p_{NH_3}^2}{p_{N_2} p_{H_2}^3}$ (c) $3^2 K_p = \frac{p_{NH_3}^2}{p_{N_2}^4}$ (d) $3^{3/2} K_p^{1/2} = \frac{p_{NH_3}^2}{p_{N_2}^4}$

22. The average speed of H_2, N_2 and O_2 gas molecules is in the order

(a) $H_2 > N_2 > O_2$ (b) $O_2 > N_2 > H_2$ (c) $H_2 > O_2 > N_2$ (d) $N_2 > O_2 > H_2$

23. The enthalpy of vaporization $\left(\Delta_{vap}H\right)$ is zero at

(a) Boyle temperature (b) critical temperature
(c) inversion temperature (d) boiling temperature.

24. The half-life of any zero-order reaction is:

(a) independent of concentration (b) proportional to inverse of concentration
(c) proportional to concentration (d) proportional to square of the concentration.

25. The molality of $(NH_4)_2SO_4$ solution that has the same ionic strength as 1 mol kg^{-1} solution of KCl is:

(a) $\frac{1}{3}$ mol kg^{-1} (b) $\frac{1}{2}$ mol kg^{-1} (c) $\frac{2}{5}$ mol kg^{-1} (d) $\frac{3}{5}$ mol kg^{-1}

26. The standard enthalpy of formation $\left(\Delta_f H^0_{300}\right)$ at 1 bar and 300 K for the formation of $CF_2ClCF_2Cl(g)$ from its constituent elements in the standard state is –900 kJ mol^{-1}. Given R = 8.3 J K^{-1} mol^{-1}, the standard internal energy of formation $\left(\Delta_f U^0_{300}\right)$ at the same pressure and temperature is:

(a) –905 kJ mol^{-1} (b) –895 kJmol^{-1} (c) 895 kJ mol^{-1} (d) 905 kJ mol^{-1}.

27. The percent transmittance of a solution having absorbance (optical density) 1.0 is:

(a) 1 (b) 10 (c) 50 (d) 99

28. The matrix which transforms $\begin{pmatrix} x \\ y \end{pmatrix}$ to $\begin{pmatrix} -y \\ -x \end{pmatrix}$ is:

(a) $\begin{pmatrix} -1 & -1 \end{pmatrix}$ (b) $\begin{pmatrix} -1 \\ -1 \end{pmatrix}$ (c) $\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$ (d) $\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$

29. A concentration cell with two hydrogen electrodes at two different pressures is depicted as

$$\begin{matrix} H_2(g)(Pt) \\ p_{H_2} = p_1 \end{matrix} \Big| HCl(aq) \Big| \begin{matrix} H_2(g)(Pt) \\ p_{H_2} = p_2 \end{matrix}$$

The potential (E_{cell}) of the cell is:

(a) $\frac{RT}{F}\ell n\frac{p_2}{p_1}$ (b) $\frac{RT}{F}\ell n\frac{p_1}{p_2}$ (c) $\frac{RT}{2F}\ell n\frac{p_2}{p_1}$ (d) $\frac{RT}{2F}\ell n\frac{p_1}{p_2}$

30. An aqueous solution containing 1 g L^{-1} of a polymer exerts osmotic pressure of 4 torr at 300K. Given R = 0.082 L atm, the molar mass (g mol^{-1}) of the polymer is:

(a) 4500 (b) 4564 (c) 4674 (d) 4800

Subjective questions

31. (a) Identify the most acidic compound from the following: CH_3-CH_3, $CH_2=CH_2$ and $CH\equiv CH$, and justify your answer. Draw overlap of the orbitals to show bonding in the most acidic compound using the concept of hybridization. **[Marks: 09]**

(b) Write a balanced chemical equation to represent acid-base reaction of orthoboric acid in water. Addition of ethylene glycol to aqueous orthoboric acid enhances its acidity. Explain the above statment using appropriate chemical equation. **[Marks: 06]**

32. (a) Draw the unit cell structure of NaCl. Calculate the limiting radius ratio of any ionic solid having NaCl like structure. **[Marks: 09]**

(b) Give molecular formula and structure of the compound formed by reaction of $Be(OH)_2$ with acetic acid. **[Marks: 06]**

33. (a) The spin-only magnetic moments of $K_3[Fe(oxalate)_3]$ and $K_3[Ru(oxalate)_3]$ are 5.91 μ_B and 1.73 μ_B, respectively. Write down their ligand field electronic configuration. Justify your answer. Atomic numbers of Fe and Ru are 26 and 44 respectively. **[Marks: 09]**

(b) Draw the structures of NO_2^+, NO_2 and NO_2^-. Arrange them in the increasing order of O–N–O bond angles **[Marks: 09]**

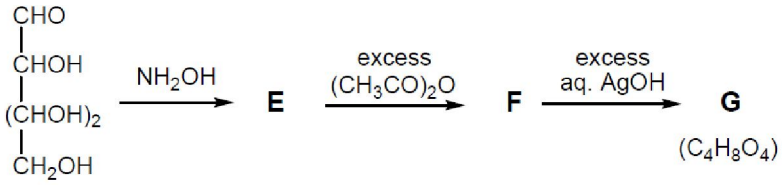
34. (a) Show with labels the splitting of d-orbitals in an octahedral ligand field. Calculate the CFSE of (i) high spin d^6 and (ii) low spin d^6 metal ions in octahedral field. **[Marks: 09]**

(b) Schematically represent orbital overlaps in metal carbonyls. Show the correct signs of the lobes. **[Marks: 06]**

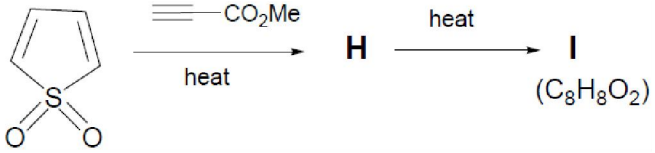
35. (a) A coordination compound is composed of one Co(III), one chloride, one sulfate and four molecules of ammonia. The aqueous solution of the compound gives no precipitate when combined with aqueous $BaCl_2$, while a white precipitate is formed with aqueous $AgNO_3$ solution. Draw its structure and explain the observations with chemical equations. **[Marks: 09]**

(b) Draw the structures of dimethylglyoxime ($DMGH_2$) and its Ni(II) complex formed in aqueous ammonia. **[Marks: 06]**

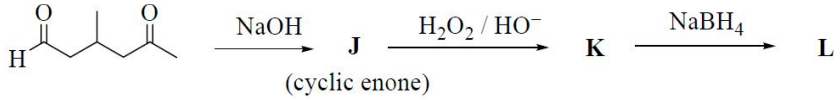
36. (a) Write the structures of **E, F** and **G** in the following scheme of reactions. **[Marks: 09]**



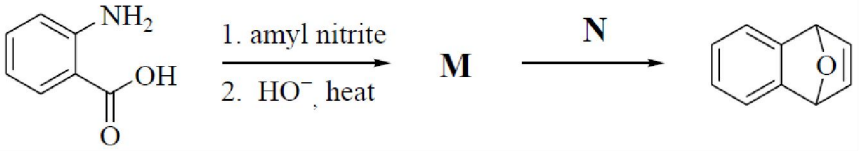
(b) Identify the structues of H and I in the following synthetic transformation **[Marks: 06]**



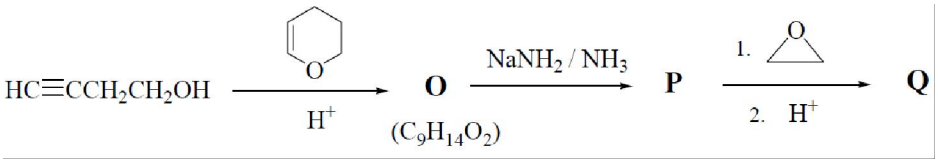
37. (a) Complete the following reaction sequence with appropriate structures of **J**, **K** and **L**. **[Marks: 09]**



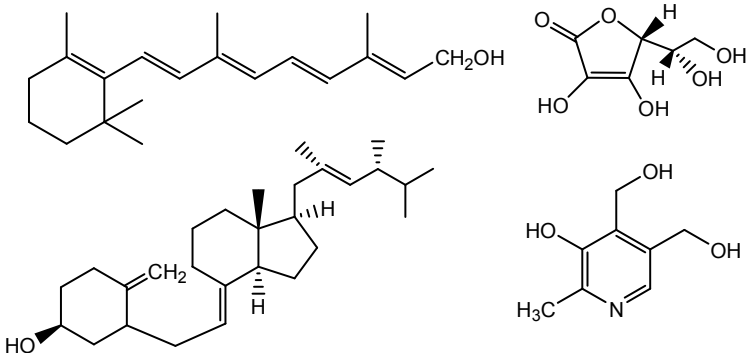
(b) Identify the structures of **M** and **N** in the following synthetic transformation **[Marks: 06]**



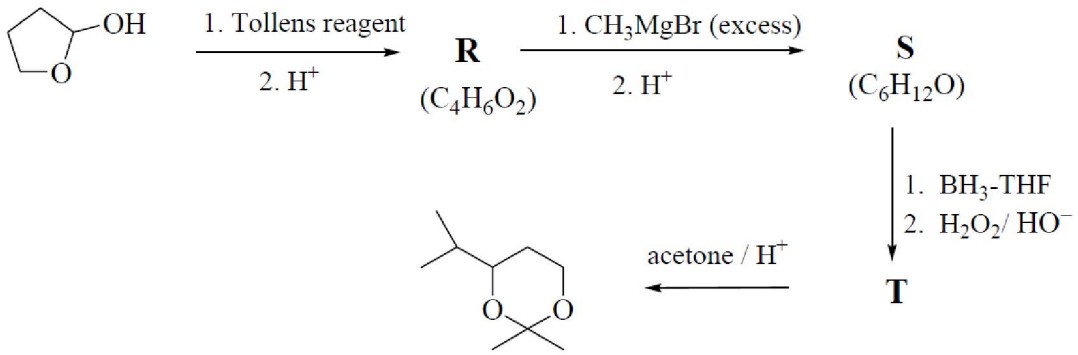
38. (a) In the following reaction scheme, write the structure of **O**, **P** and **Q** **[Marks: 09]**



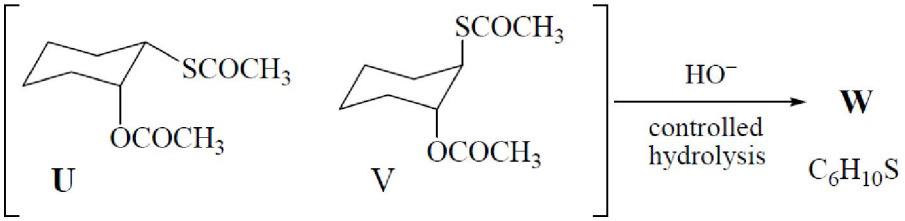
(b) Given below are structures of some natural products. Identify them as vitamin A, B_6, C and D and classify them according to their classes (isoprenoid, alkaloid, carbohydrate and steroid) **[Marks: 06]**



39. (a) Write the appropriate structures for **R**, **S** and **T** in the following scheme. **[Marks: 09]**



(b) Choose the correct stereoisomer between U and V that would furnish W on controlled hydrolysis. Write the stable conformation of W. **[Marks: 06]**



40. The mechanism of isomerization of cyclobutene (CB) to 1, 3-butadiene (BD) is as follows.

$$CB + CB \xrightarrow{k_1} CB^* + CB$$

$$CB^* + CB \xrightarrow{k_{-1}} CB + CB$$

$$CB^* \xrightarrow{k_2} CD$$

(a) Show that the rate law is $\frac{d[DB]}{dt} = \frac{k_2.k_1.[CB]^2}{k_{-1}.[CB] + k_2}$ **[Marks: 06]**

(b) The apparent first-order rate constant, $k_{app} = \frac{k_2.k_1.[CB]}{k_{-1}.[CB] + k_2}$. At the CB concentration of 1×10^{-5} mol dm^{-3}, the value of k_{app} reaches 50% of its limiting value obtained at very high concentrations of CB. Evaluate the ratio $\frac{k_2}{k_{-1}}$. **[Marks: 09]**

41. (a) The molar conductance of 0.012 mol dm^{-3} aqueous solution of chloroacetic acid is 100 Ω^{-1} cm^2 mol^{-1}. The ion conductance of chloroacetate and H^+ ions are 50 Ω^{-1} cm^2 mol^{-1} and 300 Ω^{-1} cm^2 mol^{-1}, respectively. Calculate (i) degree of dissociation and pK_a of chloroacetic acid, and (ii) H^+ ion concentration in the solution. **[Marks: 09]**

(b) Sketch the conductivity versus concentration of base curves for the titration of aqueous solutions of acetic acid (i) with NaOH, and (ii) with NH_4OH. **[Marks: 06]**

42. A solution of a free particle Schrodinger equation $\frac{-h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$ is $\psi(x) = e^{ikx} = \cos kx + i\sin kx$

(a) Derive expressions for energy 'E' and momentum 'p' of the particle. **[Marks: 09]**

(b) Using the above relations, show that the wavelength (λ) is $\frac{h}{p}$. **[Marks: 06]**

43. (a) Sketch the temperature composition phase diagram at 1 atm pressure for the ethanol-water system. **[Marks: 09]**

(i) Label all the areas in the diagram.
(ii) Indicate the temperaure at which the composition of the vapour is same as that of the liquid. What is this mixture known as?
(iii) What is the degree of freedom at the corresponding composition?
(b) Estimate the pressure necessary to melt ice at –10ºC if the molar volume of liquid water is 18.01 mL and molar volume of ice is 19.64 mL. The entropy change for the melting process is 16.3 J K^{-1}. Assume that the molar volumes and entropy change remain constant in this temperature range. [100 J = 1 L bar]. **[Marks: 06]**

44. (a) (i) Show that for 'n' moles of a van der Waals gas, $\left(\frac{\partial U}{\partial V}\right)_T = \frac{n^2 a}{V^2}$. **[Marks: 09]**

(ii) Can a gas that obeys the equation of state $p(V - nb) = nRT$ be liquefied? Explain.

(b) Consider ideal mixing of 2 moles of toluene and 2 moles of benzene at 1 atm and 300K. Calculate the values of $\Delta_{mix}V$, $\Delta_{mix}U$, $\Delta_{mix}H$, $\Delta_{mix}G$ and $\Delta_{mix}S$ for te process. ($ln\,2 = 0.69$) **[Marks: 06]**

IIT-JAM 2013 Chemistry

INSTRUCTIONS:

- **Questions 1-10 (Objective questions) carry <u>two</u> marks each, questions 11-20 (fill in the blank questions) carry <u>three</u> marks each and questions 21-30 (descriptive questions) carry <u>five</u> marks each.**
- **The marking scheme for the objective type question, is as follows:**
  (a) For each correct answer, you will be anwarded 2 (Two) marks.
  (b) For each wrong answer, you will be awarded –0.5 (Negative half) mark.
  (c) Multiple answers to a question will be treated as a wrong answer.
  (d) For each un-attempted question, you will be awarded 0(Zero) marks.
  (e) Negative marks for objective part will be carried over to total marks.
- **There is no negative marking for fill in the blank questions.**

Objective Questions

1. The most polar compound among the following is:
   (a) SF_4 (b) BF_3 (c) XeF_4 (d) SO_3

2. Which one of the following order of the carbonates is CORRECT for their decomposition temperature?
   (a) $BaCO_3 > CaCO_3 > SrCO_3 > MgCO_3$ (b) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$
   (c) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$ (d) $MgCO_3 > CaCO_3 > BaCO_3 > SrCO_3$

3. The CORRECT order of CO vibrational stretching frequency in the following complexes is
   (I) $(PF_3)_3Mo(CO)_3$ (II) $(PCl_3)_3Mo(CO)_3$ (III) $\{P(OMe)_3\}_3Mo(CO)_3$
   (a) I < II < III (b) III < II < I (c) II < I < III (d) III < I < II

4. Among the following, the ligand that BEST stablizes low oxidation state of tungsten (W) is
   (a) H_2O (b) NH_3 (c) CO (d) F^-

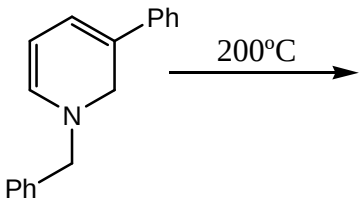
5. The function $y = x\exp\left(-x^2\right)$ has a minimum at $x = -\frac{1}{\sqrt{2}}$. The second derivative of the function at the minimum is

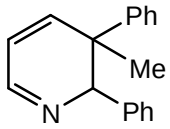
   (a) $2\sqrt{2}\exp\left(-\frac{1}{2}\right)$ (b) $-2\sqrt{2}\exp\left(-\frac{1}{2}\right)$ (c) 0 (d) $-\sqrt{2}\exp\left(-\frac{1}{2}\right)$

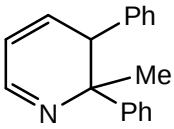
6. For a particular reaction at constant temperature, a plot of inverse of reactant concentration $\left(\frac{1}{[A]}\right)$ versus time is a straight line with a slope of 4.0×10^{-2} L mol^{-1} s^{-1}. The time required (in seconds) for 1.0 M of reactant to decrease to 0.25 M is:
   (a) 18.8 (b) 34.7 (c) 75.0 (d) 187.5

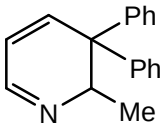
7. For a physisorption process, which one of the following statements is NOT correct?
   (a) There are van der Waals interactions between the adsorbate and the adsorbent.
   (b) The process predominates at low temperature.
   (c) The process cannot proceed beyond a monolayer
   (d) The process is reversible.

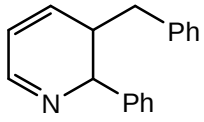
8. The product of the following reaction is



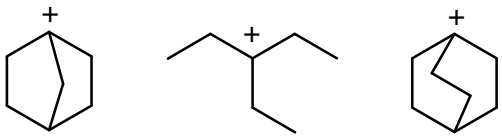
(a) 

(b) 

(c) 

(d) 

9. The CORRECT order of stability of the following carbonium ions is



(I) **(II)** **(III)**

(a) II > I > III (b) III > II > I (c) I > III > II (d) II > III > I

10. Which one of the following statements is CORRECT?
(a) Naturally occuring DNA has B-configuration.
(b) Nucleic acids are derived from proteins.
(c) Proteins store genetic information
(d) Vitamins generally act as enzymes.

Fill in the blank questions.

11. The reaction of anhydrous $FeCl_2$ with sodium-pentadienyl in ether gives an air-stable diamagnetic orange solid, which on oxidation gives an air-sensitive paramagnetic blue-green compound in solution. The blue-green compound is .....

12. CaO, VO and MnO have octahedral coordination of the metal ions in a rock-salt structure. The correct increasing order of their lattice enthalpies is .....

13. The shape of the interhalide IF_8^- is .....

14. The vapour pressures of solid and liquid chlorine are given by

$$\log_e P^{solid} = 24 - \frac{3900}{T} \text{ and } \log_e P^{liq} = 18 - \frac{2600}{T}$$

where P_{solid} and P_{liq} are the vapour pressures (in Torr) of solid and liquid chlorine near the triple point, respectively and T is the absolute temperature. The ratio of the slope of the solid-gas curve to the slope of the liquid gas curve at the triple point in the P-T diagram is .....

15. For unnormalized wave-function, $\psi(r,\theta,\phi) = \sin\theta\cos\phi\left(\frac{2r}{a_0} - \left(\frac{r}{a_0}\right)^2\right)\exp\left(-\frac{r}{a_0}\right)$, the number of radial node(s) is .....

16. A hypothetical element (atomic weight = 300) crystallizes in a simple cubic lattice. For this crystal, the first order X-ray diffraction with wavelength of 5 Å appears at an angle of 30°. The density of the crystal is ..... $g\ cm^{-3}$. [Avogadro number, $N_A = 6.02\times10^{23}$]

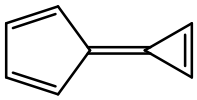
17. $MnO_4^-(aq) + Zn(s) + H_3O^+(aq) \rightarrow Mn^{2+}(aq) + Zn^{2+}(aq) + H_2O(\ell)$

For the above reaction if the equilibrium constant at 298 K is represented by 10^X, then the value of X is .....

[Given: The standard cell potential $E^0 = 2.4V$ and $\frac{2.303RT}{F} = 0.06V$ at 298K]

18. The rotational energy barrier between the most stable and the least stable conformations of 2, 3-dimethylbutane along C2–C3 bond is .....kcal mol^{-1}.
[Given: The energies (kcal mol^{-1}) for H/CH_3 eclipsing = 1.8, CH_3/CH_3 eclipsing = 2.9 and CH_3/CH_3 gauche = 0.9]

19. The number of peaks or signals in ^1H NMR of N, N-dimethylformamide (DMF) at 25°C is .....

20. 

calixene

Calixene is a polar hydrocarbon with a high dipole moment. The most stable dipolar canonical structure is .....

Descriptive questions

21. A mixture of C_3H_8 and oxygen in 1L closed vessel has an internal pressure of 4 atm at 100°C. When the mixture is ignited, the reaction produces CO_2(g) and H_2O(g) until all oxygen is consumed. After the reaction, pressure of the vessel is 4.2 atm at the same temperature. Calculate the weight of oxygen present before the reaction. [Gas constant, R = 0.082 L atm mol^{-1} K^{-1}].

22. The following reaction is carried out at 1 atm and 300 K

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$

ΔU for the above reaction is 550 kJ. Assuming ideal gas behaviour for H_2 and O_2, calculate the value of ΔH. The value of gas constant, R = 0.082L atm $mol^{-1}K^{-1}$ = 8.314 $mol^{-1}K^{-1}$.
[Given: The volume of 1 mole of liquid water is 18 mL under the above reaction condition]

23. At 298K, calculate the solubility of metal sulfide, MS(s), in a saturated solution of H_2S where the concentration of H_2S and pH are maintained at 0.1 M and 3.0, respectively
Given at 298 K,

$H_2S(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$ $\quad K = 10^{-7}$

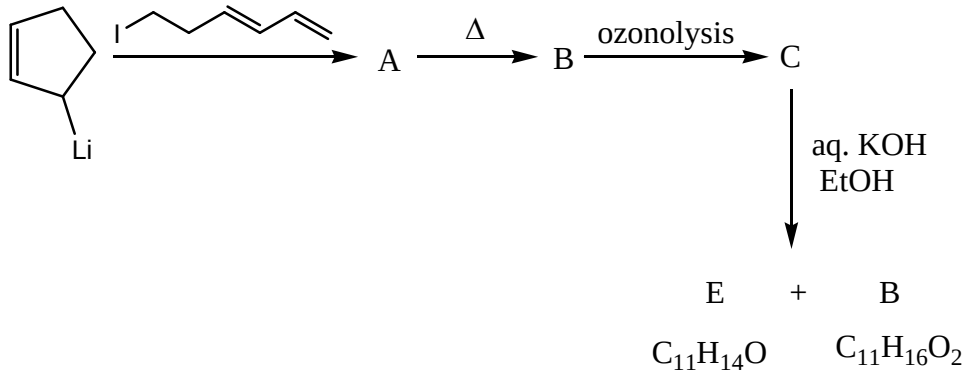
$MS(s) + H_2O(\ell) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-(aq)$ $\quad K = 5 \times 10^{-19}$

24. For each of the following metallo-proteins identify the metal-ion at the active-site and the function of the proteins:
deoxy-hemoglobin, deoxy-myoglobin, oxy-hemocyanin, cytochrome-c and carbonic anhydrase.

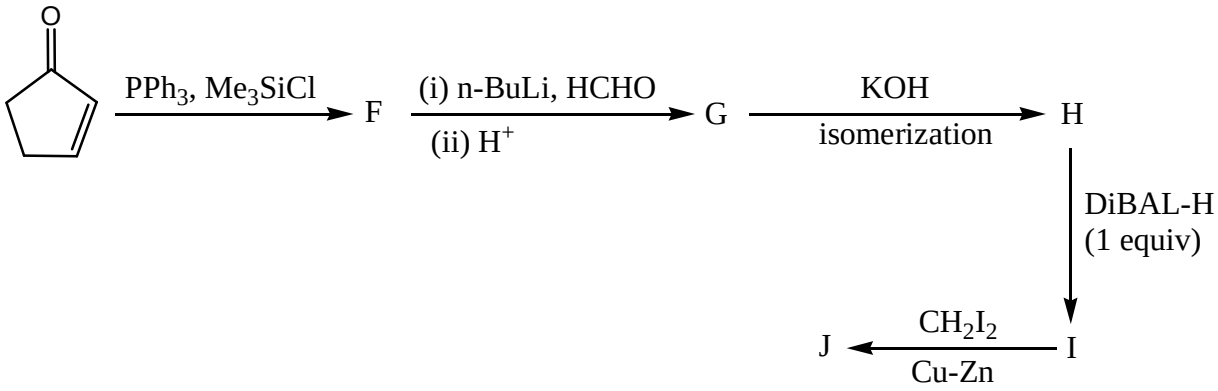
25. A solution containing 250 ppm of $CuSO_4.5H_2O$ (formula weight = 250) has an absorbance of 0.1 measured in 1 cm cell at 600 nm. Calculate the molar absorptivity (ε) of $CuSO_4.5H_2O$ in L $M^{-1}cm^{-1}$. When 25 mL of Na_2EDTA (aq) solution is titrated against Na_2EDTA (aq) solution, it consumes at 50 mL of Na_2EDTA(aq) solution. Calculate the concentration of Na_2EDTA(aq) solution in moles L^{-1}.

26. Assume the complex $[Ni(PPh_3)_2(SCN)_2]$ is paramagnetic. The analogous complex of Pd(II) is diamagnetic. Draw all the probable isomers for both the complexes considering SCN^- is an ambidentate ligand.

27. Write the structues of A to E in the following reaction sequence:

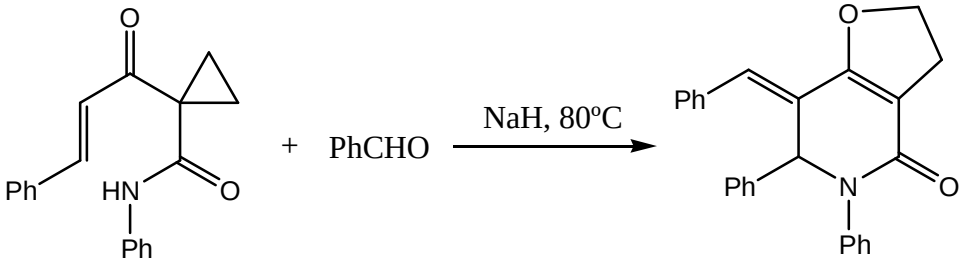


28. Write the structures of F to J in the following reaction scheme:

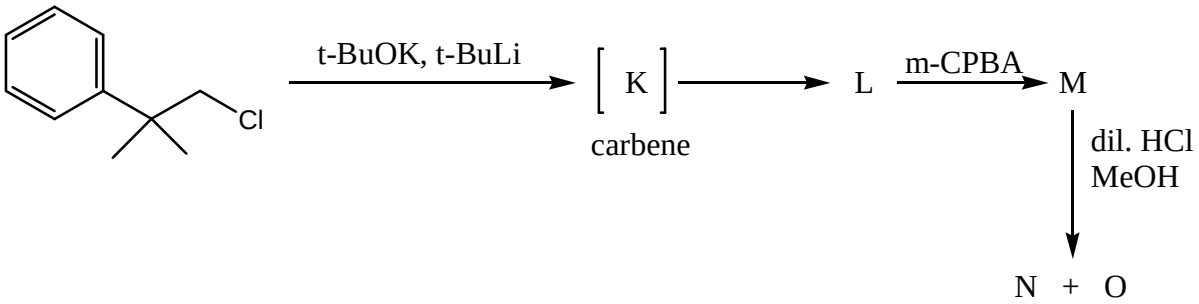


[DiBAL–H = diisobutylaluminium hydride]

29. Propose a mechanism for the following reaction. Show stepwise correct reactive intermediates



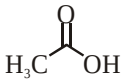
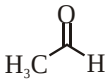
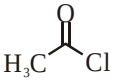
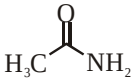
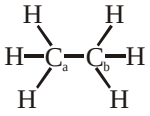
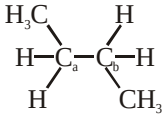
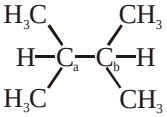
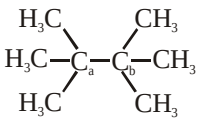
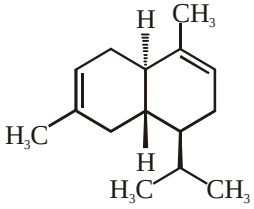
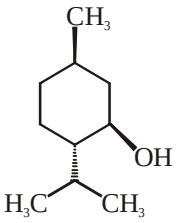
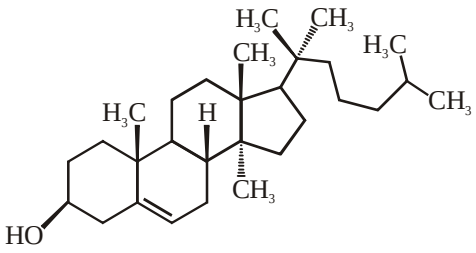
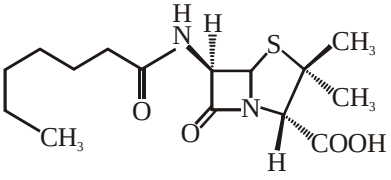
30. Complete the following reaction sequence and write structures of K to O.



IIT-JAM-2014 (CHEMISTRY) (CODE-A)

PART-I : OBJECTIVE QUESTIONS

Q. 1 - Q. 10 carry one mark each.

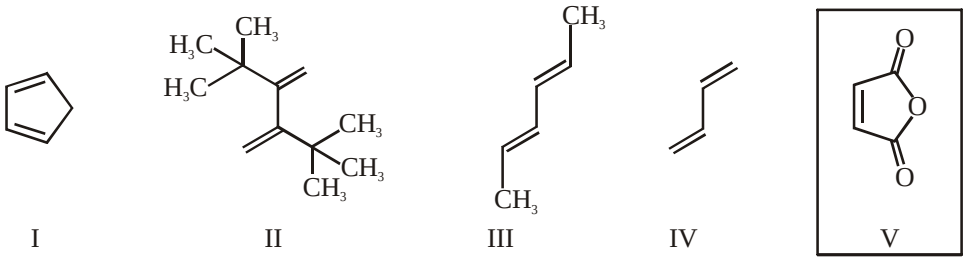
1. For square matrices M and N, if MN = M and NM = N, then:
   (a) $M^2 = M$ and $N^2 = N$ (b) $N^2 \neq N$ and $M^2 = M$
   (c) $M^2 \neq M$ and $N^2 \neq N$ (d) $M^2 \neq M$ and $N^2 = N$
2. The energy of an electron in a hydrogenic atom with nuclear charge Z varies as:
   (a) Z (b) Z^2 (c) 1/Z (d) $1/Z^2$
3. The carbonyl stretching frequency ($\nu_{C=O}$) is highest for:
   (a)  (b)  (c)  (d) 
4. The homolytic breaking of the $C_a - C_b$ bond is easiest in:
   (a)  (b)  (c)  (d) 
5. Tollen's test will be negative for:
   (a) Glucose (b) Mannose (c) Sucrose (d) Galactose
6. Which one among the following is a sesquiterpene?
   (a)  (b) 
   (c)  (d) 
7. The predicted geometry of TeF_4 by **VSEPR theory** is:
   (a) Octahedral (b) Square planar (c) Tetrahedral (d) Trigonal bipyramidal
8. Among the following, the isoelectronic pair is:
   (a) NO and CO (b) O_2^- (superoxide anion) and NO^-
   (c) NO^+ and CO (d) O_2^- (superoxide anion) and NO^+

9. The metal ion of an enzyme involved in hydration of CO_2 is:
(a) Cu(II) (b) Fe(II) (c) Mg(II) (d) Zn(II)

10. Among the following, the element having maximum inert pair effect is:
[Given : Atomic number of Ge = 30, Pb = 82, Si = 14 and Sn = 50]
(a) Ge (b) Pb (c) Si (d) Sn

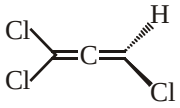
Q.11 - Q.35 carry two marks each:

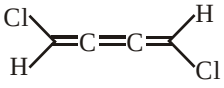
11. The reactivity of compounds I-IV with maleic anhydride (V) follows the order:

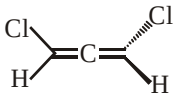


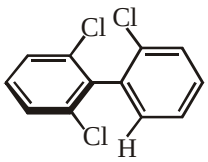
(a) I < II < III < IV (b) II < IV < III < I
(c) II < I < III < IV (d) II < I < IV < III

12. Which one among the following molecules is chiral?

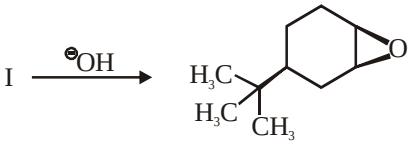
(a) 

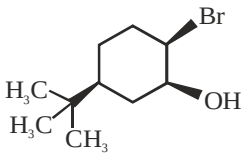
(b) 

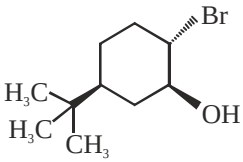
(c) 

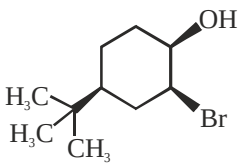
(d) 

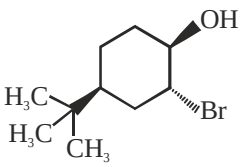
13. Identify the starting material I in the given reaction.



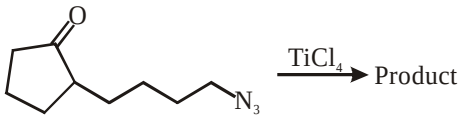
(a) 

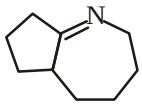
(b) 

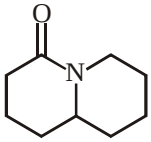
(c) 

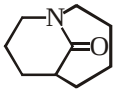
(d) 

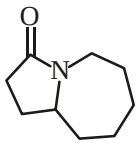
14. The major product for the following reaction is:



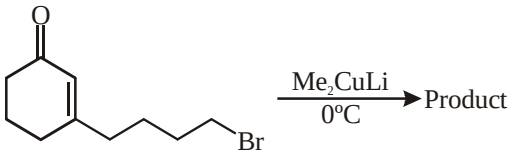
(a) 

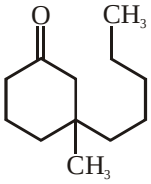
(b) 

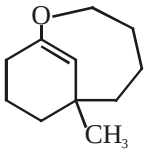
(c) 

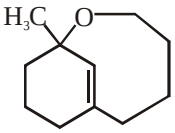
(d) 

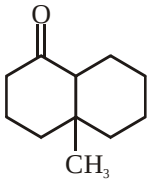
15. The structure of the major product in the following reaction is:



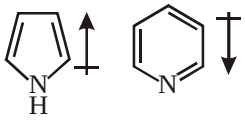
(a) 

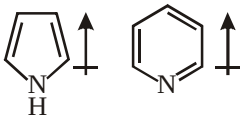
(b) 

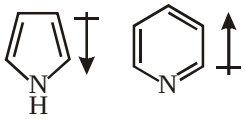
(c) 

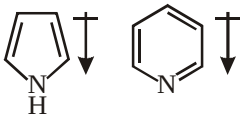
(d) 

16. The correct orientation of dipoles in pyrrole and pyridine is:

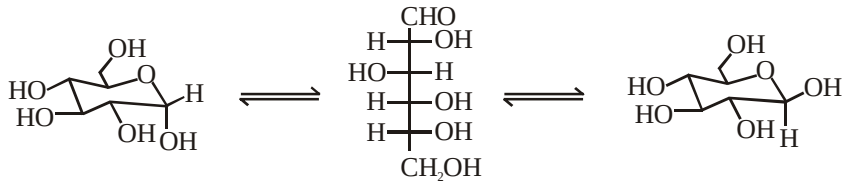
(a) 

(b) 

(c) 

(d) 

17. Specific rotations of freshly prepared aqueous solutions of I and II are +112 and +18.7, respectively. On standing the optical rotation of aqueous solution of I slowly decreases to give a final value of +52.7 due to equilibrium with II. Under this state of equilibrium, what is the ratio II : I?

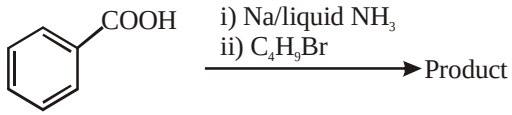


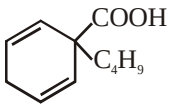
I
$[\alpha]_D^{25} = +112$

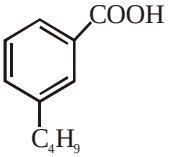
II
$[\alpha]_D^{25} = +18.7$

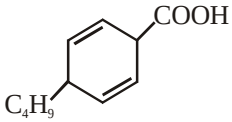
(a) 0.57 (b) 1.00 (c) 1.75 (d) 5.9

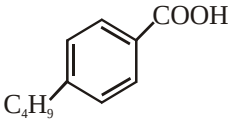
18. The major product formed in the following reaction is:



(a) 

(b) 

(c) 

(d) 

19. In boron neutron capture therapy, the initial boron isotope used and the particle generated after neutron capture respectively are:

(a) ^{11}B and α particle (b) ^{10}B and α particle

(c) ^{11}B and β particle (d) ^{10}B and β particle

20. The number of α and β particle(s), generated in the following radioactive decay process, are:

$$^{238}_{92}U \rightarrow {}^{234}_{92}U$$

(a) one α and two β particles (b) two α and one β particles

(c) one α and four β particles (d) no α and four β particles

21. In the measurement of hardness of water by complexometric titration, identify P and Q in the following equation.

$[P]^-$	+	$[H_2Y]^{2-}$	$\rightarrow$	$[Q]^{2-}$	+	$[HIn]^{2-}$	+	H^+
red		colourless		colourless		blue		

(a) P = MgY, Q = MgIn (b) $P = MgY_2$, $Q = MgIn_2$

(c) $P = MgIn_2$, $Q = MgY_2$ (d) P = MgIn, Q = MgY

22. An aqueous solution of hemoglobin has a molar absorptivity value of 18,600 L mol^{-1} cm^{-1} for an absorbance value of 0.1 at 540 nm (Given : cell thickness = 1cm). The concentration (in μM) of the hemoglobin solution is:

(a) 0.537 (b) 5.37 (c) 53.7 (d) 537.0

23. The electronic transitions responsible for the colour of $K_2Cr_2O_7$ and porphine in their solid state respectively are:

(a) $d \rightarrow d; \pi \rightarrow \pi^*$ (b) $M \rightarrow L$ charge transfer; $\pi \rightarrow \pi^*$

(c) $L \rightarrow M$ charge transfer; $\pi \rightarrow \pi^*$ (d) $L \rightarrow M$ charge transfer; $d \rightarrow d$

24. The correct order of M–C(M = Ti, V, Cr and Mn) bond stretching frequency is:
(Given: Atomic number of Ti = 22, V = 23, Cr = 24 and Mn = 25)

(a) $[V(CO)_6]^- < Cr(CO)_6 < [Mn(CO)_6]^+ < [Ti(CO)_6]^{2-}$

(b) $[Ti(CO)_6]^{2-} < [V(CO)_6]^- < Cr(CO)_6 < [Mn(CO)_6]^+$

(c) $[Mn(CO)_6]^+ < Cr(CO)_6 < [V(CO)_6]^- < [Ti(CO)_6]^{2-}$

(d) $[Mn(CO)_6]^+ < [V(CO)_6]^- < Cr(CO)_6 < [Ti(CO)_6]^{2-}$

25. For the following reactions, the metal complexes X and Y are:

(i) $Ni(s) \xrightarrow[1\ atm\ /\ 25^oC]{CO(g)} X$

(ii) $FeCl_2 \xrightarrow{2NaC_5H_5} Y$

(a) $X = Ni(CO)_4$; $Y = Fe(\eta^5\text{-}C_5H_5)_2$ (b) $X = Ni(CO)_4$; $Y = Fe(\eta^1\text{-}C_5H_5)_2$

(c) $X = Ni(CO)_5$; $Y = Fe(\eta^5\text{-}C_5H_5)_2$ (d) $X = Ni(CO)_6$; $Y = Fe(\eta^1\text{-}C_5H_5)_2$

26. The correct order of crystal field strength is : (Given: en = ethylenediamine)

(a) $Cl^- < H_2O < en < (\eta^5\text{-}C_5H_5)^-$ (b) $H_2O < Cl^- < (\eta^5\text{-}C_5H_5)^- < en$

(c) $H_2O < (\eta^5\text{-}C_5H_5)^- < en < Cl^-$ (d) $en < Cl^- < H_2O < (\eta^5\text{-}C_5H_5)^-$

27. The carbon-oxygen bond in an organic compound absorbs electromagnetic radiation of frequency 6×10^{13} Hz. This frequency corresponds to the region:

(a) Infrared (b) Microwave (c) Ultraviolet (d) Visible

28. According to the equipartition principle of energy, the molar heat capacity at constant volume for $CO_2(g)$, $SO_2(g)$ and $H_2O(g)$ follows the trend:

(a) $CO_2 = SO_2 = H_2O$ (b) $CO_2 > SO_2 = H_2O$

(c) $H_2O > SO_2 = CO_2$ (d) $CO_2 = SO_2 > H_2O$

29. $\left[\frac{-h^2}{(8\pi^2 m)}\frac{d^2}{dx^2}+\frac{h^2\alpha^2x^2}{(2\pi^2 m)}\right]\exp(-\alpha x^2)=C\frac{h^2}{(4\pi^2)}\exp(-\alpha x^2)$, where h, π, m and α are constants. Then C is:

(a) $2\alpha/m$ (b) $\alpha/2m$ (c) α/m (d) α^2/m

30. Among Ar, NH_4Cl, HF and HCl, the strength of interatomic / intermolecular forces follows the order:

(a) $NH_4Cl > HF > HCl > Ar$ (b) $HF > HCl > Ar > NH_4Cl$

(c) $HCl > Ar > NH_4Cl > HF$ (d) $Ar > NH_4Cl > HF > HCl$

31. The number of degrees of freedom in the homogeneous liquid region of a two component system with a eutectic point, at one atmosphere pressure, is:

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

32. The ionic strength of 0.1 M aqueous solution of $Fe_2(SO_4)_3$ is:

(a) 0.1 M (b) 0.65 M (c) 1.3 M (d) 1.5 M

33. If the transport number of Na^+ is 0.463 (dilute solution of NaCl in methanol), the transport number of H^+ (dilute solution of HCl in methanol) is:

(Given, Λ^∞ (NaCl in methanol) = 96.9 ohm^{-1} cm^2 mol^{-1} and Λ^∞ (HCl in methanol) = 192 ohm^{-1} cm^2 mol^{-1})

(a) 0.27 (b) 0.46 (c) 0.54 (d) 0.73

34. Charcoal (1 gram) of surface area 100 m^2 per gram, absorbs 60mg of acetic acid from an aqueous solution at 25ºC and 1 atmosphere pressure. The number of moles of acetic acid adsorbed per cm^2 of charcoal surface is:

(a) 10^{-2} (b) 10^{-6} (c) 10^{-5} (d) 10^{-9}

35. The change in entropy for the following transformations is respectively: (+ indicates increase, –indicates decrease and 0 indicates no change)

(i) $SO_2Cl_2(g) \xrightarrow{\Delta} SO_2(g) + Cl_2(g)$

(ii) $nCH_2 = CH_2(g) \xrightarrow{\text{Catalyst}} \left[CH_2-CH_2\right]_n(s)$

(iii) $I_2(s) \xrightarrow[\text{1 atmosphere}]{\Delta} I_2(v)$

(iv) Adiabatic reversible expansion of an ideal gas

(a) +, –, 0, + (b) +, –, 0, 0 (c) –, +, +, 0 (d) +, –, +, 0

PART-II: DESCRIPTIVE QUESTIONS

Q.36 – Q.43 carry five marks each.

36. Using crystal field theory (CFT), for the $[Co(NH_3)_6]^{3+}$ ion

(a) draw the d-orbital splitting including their orbital labels (designations) and show their electron occupancy.

(b) calculate the crystal field stabilization energy (ignore pairing energy) and spin-only magnetic moment values. (Given : atomic number of Co = 27).

37. (a) Write the correct order of lattice energy for LiX, X = F, Cl, Br and I.

(b) A first order reflection from (111) plane is observed for LiX with $2\theta = 24.6^{o}$ (X-ray of wavelength 1.54Å). Assuming LiX to be a cubic crystal system, calculate the length of the side of the unit cell in Å.

38. For the reaction:

$$2NO + 2H_2 \xrightarrow{700^{o}C} N_2 + 2H_2O$$

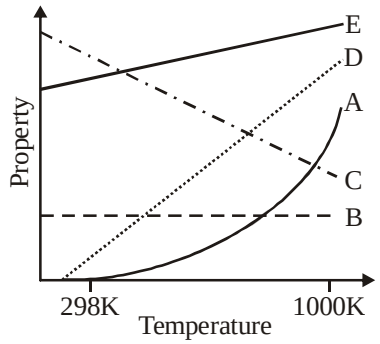
(i) Write the expression for the rate of the reaction in terms of the change in concentrations of NO and H_2O.

(ii) Given the following data for the above reaction, find the order of the reaction with respect to (a) NO and (b) H_2 and the rate constant of the reaction along with the proper unit.

	$[NO]_{t=0}\,(mol\,dm^{-3})$	$[H_2]_{t=0}\,(mol\,dm^{-3})$	Intial rate $(mol\,dm^{-3}s^{-1})$
Experiment 1	0.025	0.01	2.4×10^{-6}
Experiment 2	0.025	0.005	1.2×10^{-6}
Experiment 3	0.0125	0.01	0.6×10^{-6}

39. The vapour pressure of benzene is 5333 Pa at 7.6°C and 53330 Pa at 60.6°C. Calculate the heat of vapourization of benzene and the normal boiling point of benzene.

40. The following graph represents the dependence of certain properties I to V (given below) as a function of temperature.



Property

I The enthalpy change of a gas phase reaction in which the sum of the number of moles of products is greater than the sum of the number of moles of reactants

II The osmotic pressure of an ideal solution at a given concentration

III The standard Gibbs free energy of formation of metal oxides

IV The molar heat capacity at constant volume for a an ideal gas, as predicted by the equipartition of energy

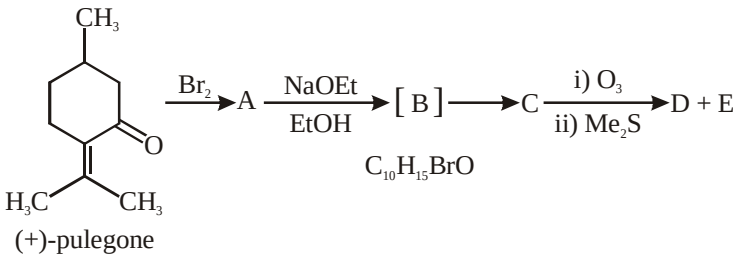
V The rate constant of a reaction with E_a = 100 kJ mol^{-1}

The lines / curves A, B, C, D and E corresponding to the appropriate property are:

Answer:

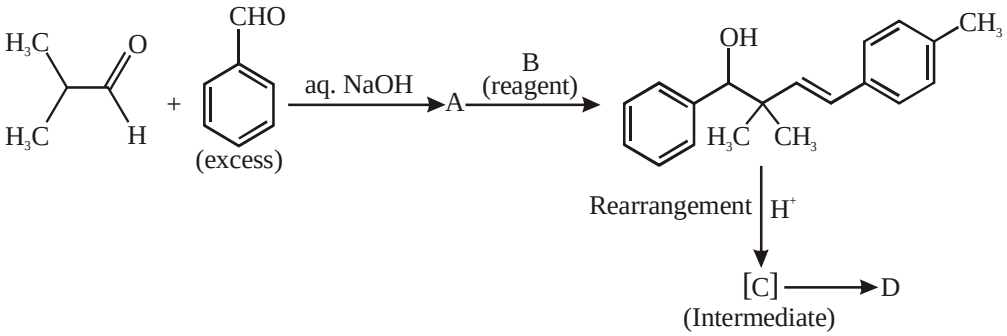
Property	Line/Curve
I	
II	
III	
IV	
V	

41. Draw the structures A-E for the given transformation:



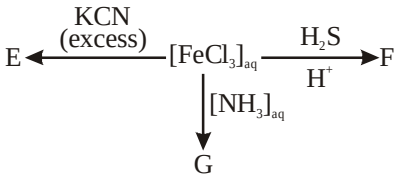
(+)-pulegone

42. In the reaction sequence given below, draw the structures of A, C, D and reagent B.



43. (a) How many ^1H NMR signals are expected for 2-chlorobut-2-ene? (ignore spin-spin coupling)

(b) Write down the iron containing chemical species, E, F and G in the following reactions.



IIT-JAM-2014 (CHEMISTRY) (CODE-A)

ANSWER KEY

1. (a)	**2.** (b)	**3.** (c)	**4.** (d)	**5.** (c)
6. (a)	**7.** (d)	**8.** (c)	**9.** (d)	**10.** (b)
11. (b)	**12.** (c)	**13.** (d)	**14.** (b)	**15.** (d)
16. (a)	**17.** (c)	**18.** (a)	**19.** (b)	**20.** (a)
21. (d)	**22.** (b)	**23.** (c)	**24.** (c)	**25.** (a)
26. (a)	**27.** (a)	**28.** (b)	**29.** (c)	**30.** (a)
31. (c)	**32.** (d)	**33.** (d)	**34.** (d)	**35.** (d)

IIT-JAM-2014 (CHEMISTRY) (CODE-A)

ANSWER KEY

1. (a)	**2.** (b)	**3.** (c)	**4.** (d)	**5.** (c)
6. (a)	**7.** (d)	**8.** (c)	**9.** (d)	**10.** (b)
11. (b)	**12.** (c)	**13.** (d)	**14.** (b)	**15.** (d)
16. (a)	**17.** (c)	**18.** (a)	**19.** (b)	**20.** (a)
21. (d)	**22.** (b)	**23.** (c)	**24.** (c)	**25.** (a)
26. (a)	**27.** (a)	**28.** (b)	**29.** (c)	**30.** (a)
31. (c)	**32.** (d)	**33.** (d)	**34.** (d)	**35.** (d)

CAREER ENDEAVOUR
ACADEMY PRIVATE LIMITED
Best Institute for CSIR-UGC-NET/JRF|GATE|IIT-JAM

IIT JAM CHEMISTRY-CY 2015

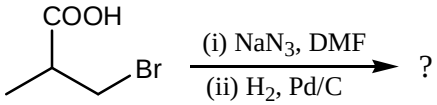
Question Paper

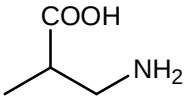
SECTION-A : MCQ

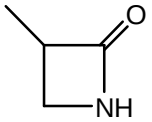
1. The first row transition metal complexes having tetrahedral geometry are high-spin due to

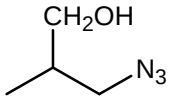
(a) $\Delta_t > P$ (b) $\Delta_t < P$ (c) $\Delta_t = P$ (d) $\Delta_t > \Delta_0$

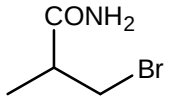
2. The major product formed in the following reaction is



(a) 

(b) 

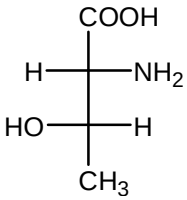
(c) 

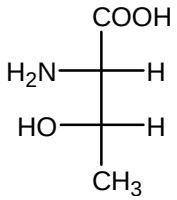
(d) 

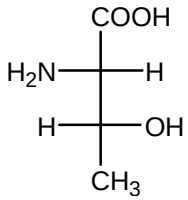
3. Which one of the following is an identity matrix?

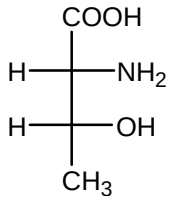
(a) $\begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$ (b) $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ (c) $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ (d) $\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$

4. The structure of (2S, 3R)-2-amino-3-hydroxy butanoic acid is

(a) 

(b) 

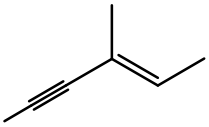
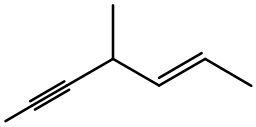
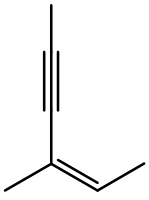
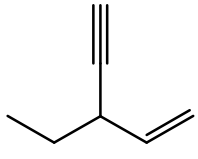
(c) 

(d) 

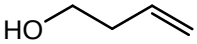
5. The intermolecular van der waals potential is inversely proportional to r^6. The corresponding force is proportional to

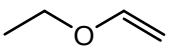
(a) $\frac{1}{r^5}$ (b) $\frac{1}{r^6}$ (c) $\frac{1}{r^7}$ (d) $\frac{1}{r^{12}}$

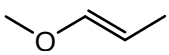
6. The ene-yne that produces a chiral compound upon treatment with Lindlar's catalyst is

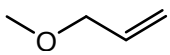
(a)  (b)  (c)  (d) 

7. An organic compound $P(C_4H_8O)$ is positive to Bayer's test, but inert to sodium metal. On treatment with conc. HCl, P gives CH_3CH_2Cl and CH_3CHO. The structure of P is

(a) 

(b) 

(c) 

(d) 

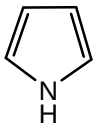
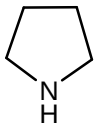
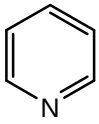
8. Low-spin iron (III) centre is present in

(a) deoxy form of hemoglobin (b) oxy form of hemoglobin
(c) hemocyanin (d) carbonic anhydrase

9. A fliter paper moistened with cadmium acetate solution turns yellow upon exposure to H_2S. The transition responsible for the yellow colour is
(a) d-d (b) metal-to-ligand charge transfer
(c) ligand-to-metal charge transfer (d) $\sigma - \sigma^*$

10. The species responsible for the superacidity of SbF_5-HSO_3F system is
(a) HSO_3F (b) SbF_5 (c) HF (d) $H_2SO_3F^+$

11. The correct order of the pKa values for the conjugate acids of heterocyclic compounds given below is

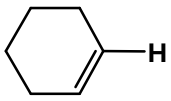
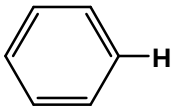
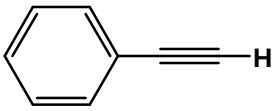
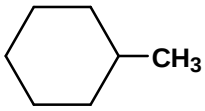
(I)  (II)  (III)  (IV) 

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

12. The species having trigonal pyramidal shape is
(a) NO_3^- (b) CO_3^{2-} (c) BrF_3 (d) SO_3^{2-}

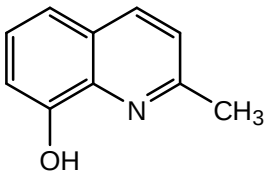
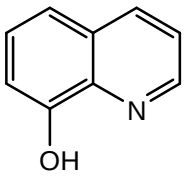
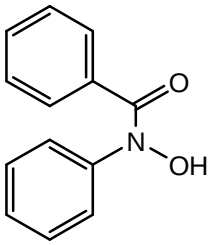
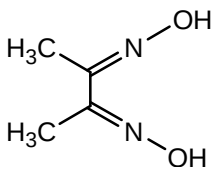
13. The Volhard method is used for the estimation of
(a) cyanide ion by titration with silver nitrate (b) silver ion directly
(c) oxygen in water (d) glucose in blood

14. The correct order of the ^1H NMR chemical shift values (δ) for the indicated hydrogens (in bold) in the following compounds is

(I)  (II)  (III)  (IV) 

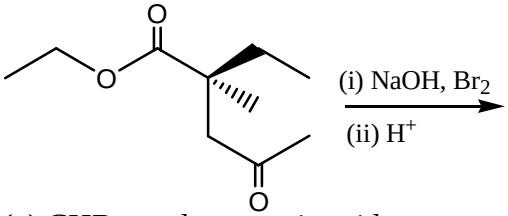
(a) I > II > III > IV (b) II > I > III > IV (c) III > II > I > IV (d) II > III > IV > I

15. The reagent 'oxine' commonly used in analytical chemistry is

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

16. The correct statement about ionization potential (IP) is
(a) non-metallic character of an element decereases as teh IP increases
(b) IP decreases down the group in the periodic table
(c) second IP of Ca is larger than second IP of K
(d) IP decreases on going from left to right in the periodic table.

17. The set of products formed in the following reaction is

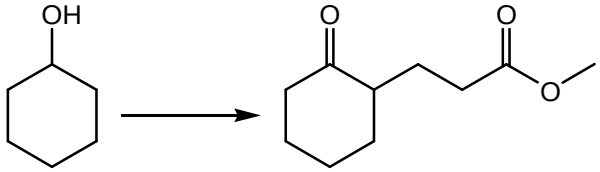


(a) $CHBr_3$ and a racemic acid (b) $CHBr_3$ and a chiral acid
(c) $CHBr_3$ and a racemic ester (d) CH_2Br_2 and a chiral ester

18. The normal spinel among the following mixed metal-oxides is
(a) $CoFe_2O_4$ (b) $NiFe_2O_4$ (c) $CuFe_2O_4$ (d) $ZnFe_2O_4$

19. The ground state term for a free ion with $3d^7$ configuration is
(a) $^4F_{3/2}$ (b) $^4F_{9/2}$ (c) $^4F_{1/2}$ (d) $^4F_{5/2}$

20. The correct set of reagents required for the following transformation is



(a) (i) CrO_3; (ii) acrylonitrile; (iii) H_3O^+
(b) (i) O_2 ; (ii) methyl acrylate
(c) (i) CrO_3 ; (ii) NaOMe/MeOH, methyl acrylate; (iii) H_3O^+
(d) (i) H_2O; (ii) methyl acrylate.

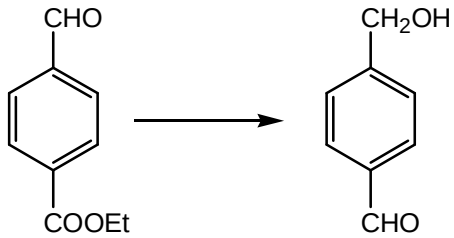
21. The concentration of K^+ ion inside a biological cell is 20 times higher than outside. The magnitude of potential difference between the two sides is [Given : 2.303 RT/F = 59 mV]
(a) 0 mV (b) 26 mV (c) 77 mV (d) 177 mV

22. At 25°C, the solubility product (K_{sp}) of CaF_2 in water is 3.2×10^{-11}. The solubility (in mole per kg of water) of the salt at the same temperature (ignore ion pairing) is
(a) 4.0×10^{-6} (b) 3.2×10^{-4} (c) 2.5×10^{-4} (d) 2.0×10^{-4}

23. The complex that is expected to show orbital contribution to the overall magnetic moment is
(a) $\left[Cr(CN)_6\right]^{3-}$ (b) $\left[Co(H_2O)_6\right]^{2+}$ (c) $\left[Ni(en)_3\right]^{2+}$ (d) $\left[Cu(NH_3)_6\right]^{2-}$

24. The correct order of the fundamental vibrational frequencies of the following diatomic molecules is
(a) $^1H^{35}Cl > {}^1H^{37}Cl > {}^2D^{35}Cl$ (b) $^2D^{35}Cl > {}^1H^{37}Cl > {}^1H^{35}Cl$
(c) $^1H^{37}Cl > {}^1H^{35}Cl > {}^2D^{35}Cl$ (d) $^1H^{37}Cl > {}^2D^{35}Cl > {}^1H^{35}Cl$

25. Identify the correct reagents required for the following transformation



(a) (i) $NaBH_4$; (ii) H_3O^+
(b) (i) $LiAlH_4$; (ii) H_3O^+
(c) (i) $HOCH_2CH_2OH$, H^+; (ii) $LiAlH_4$; (iii) H_3O^+
(d) (i) $HSCH_2CH_2SH$, H^+; (ii) $LiAlH_4$; (iii) H_3O^+

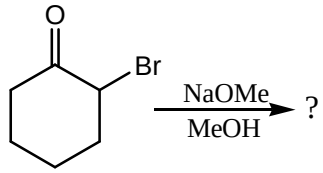
26. For an isothermal free expansion of an ideal gas into vacuum, which one of the following set of values is correct?
(a) $\Delta U = 0, q > 0, w < 0$ (b) $\Delta U > 0, q > 0, w = 0$
(c) $\Delta U = 0, q = 0, w = 0$ (d) $\Delta U < 0, q = 0, w < 0$

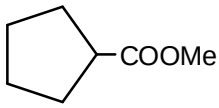
27. The kinetics of the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ in liquid bromine medium was measured independently for three different initial concentrations of N_2O_5 : 0.11, 0.07 and 0.05 mol L^{-1}. The half-life of the reaction was found to be 4.5 hours for all these concentrations. The order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 0.5

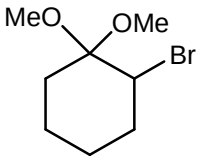
28. Which of the following statements are correct for S_NAr reaction?
(i) Follows second order kinetics
(ii) $K_H/K_D > 1$
(iii) Involves carbanion-type inermediate
(iv) Involves two transition states
(a) (i) and (ii) only (b) (ii) and (iii) only (c) (i), (iii) and (iv) only (d) (i) and (iii) only

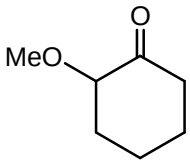
29. According to the equipartition principle, the predicted high temperature limiting value of the molar heat capacity at constant volume for C_2H_2 is
(a) 5.5 R (b) 6.0 R (c) 9.0 R (d) 9.5 R

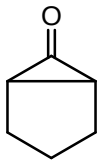
30. The major product formed in the following reaction is



(a) 

(b) 

(c) 

(d) 

SECTION-B : MSQ

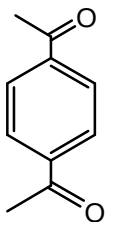
1. If $\hat{x} = xX$ and $\hat{p}_x = \frac{h}{2\pi i}\frac{d}{dx}$, then the value(s) of $\hat{p}_x\hat{x} - \hat{x}\hat{p}_x$ is/are

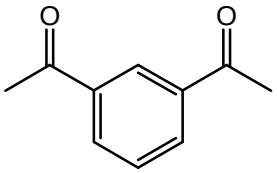
(a) $\frac{\hbar}{i}$ (b) $-i\hbar$ (c) 0 (d) $\frac{i}{\hbar}$

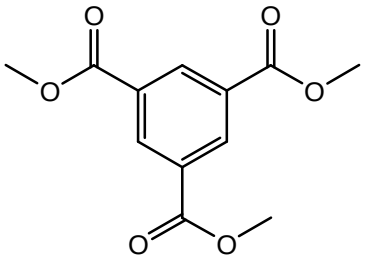
2. The common feature(s) of Rb^+, Kr and Br^- is/are that they
(a) have same numbe of valence electrons
(b) have same magnitude of effective nuclear charge
(c) have same magnitude of first ionization potential
(d) are isoelectronic species

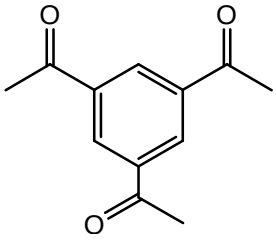
3. The characteristics of the blue solution of sodium in liquid ammonia is/are
(a) diamagnetic (b) paramagnetic
(c) reducing in nature (d) conducts electricity

4. Which of the following compound(s) show(s) only two signals in ^1H NMR and a strong IR band at ~ 1690 cm^{-1}.

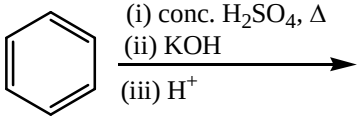
(a) 

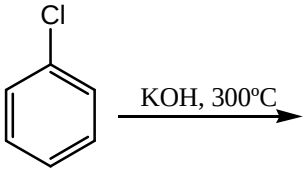
(b) 

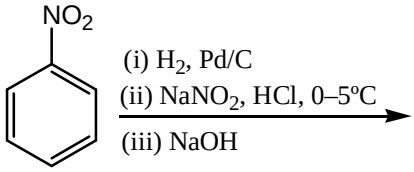
(c) 

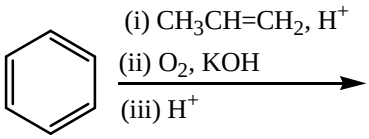
(d) 

5. The reaction(s) which give(s) phenol is/are

(a) 

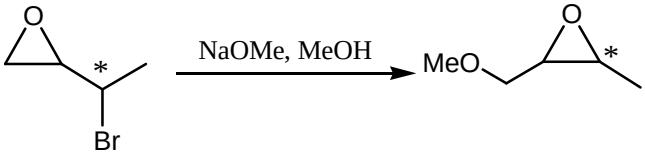
(b) 

(c) 

(d) 

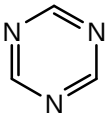
6. At what angle(s) of incidence, X-rays of wavelength 5.0Å will produce diffracted beam from the (110) planes in a simple cubic lattice with a = 10Å?
(a) 6.8° (b) 10.2° (c) 20.7° (d) 45.0°

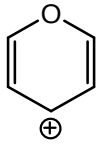
7. Which of the following statement(s) is/are true about the reaction given below?

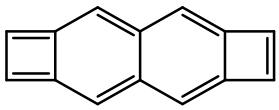


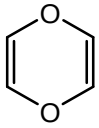
(a) it involves a carbocation intermediate
(b) rearrangement is due to S_N1 reaction mechanism.
(c) it proceeds via a concerted S_N2 pathway
(d) it involves neighbouring group participation.

8. Which of the following species is/are aromatic in nature?

(a) 

(b) 

(c) 

(d) 

9. Which of the following statement(s) is/are true about the transition metal-alkene complexes?
(a) Back-bonding weakenes the double bond of the alkene
(b) σ-bonding and back-bonding synergistically strengthen metal-alkene interaction
(c) Electron-withdrawing substituents on alkene reduce back-bonding
(d) π-acidic co-ligands on metal strengthen back-bonding

10. Which of the following thermodynamic relation(s) is/are correct?

(a) $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$ (b) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ (c) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (d) $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

SECTION-C : NAT

1. In the gas phase, the ratio of excluded volume to molecular volume for a spherical molecule is _____

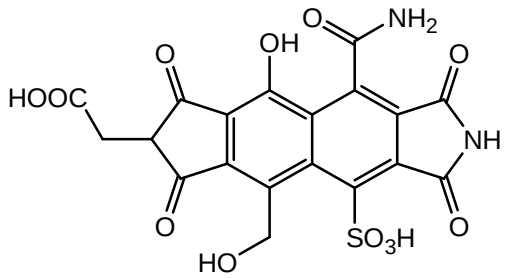
2. The pK_a values of lysine are 2.18, 8.95 and 10.79. The isoelectric point of lysine is _____

3. The amount (in grams) of potassium dichromate (MW = 294) present in 75 mL of 0.16 M aqueous solution is _____

4. Given that the expected spin-only magnetic moment for $(Et_4N)_2[NiCl_4]$ is 2.83 μ_B, the total number of unpaired electrons in this complex is _____

5. Given that the crystal field stabilization energy for $\left[Co\left(H_2O\right)_6\right]^{2+}$ is 7360 cm^{-1}, the calculated value of Δ_0 in kJ mol^{-1} is _____

6. The amount (in grams) of NaOH (MW = 40) required for complete neutralization of one mole of the following compound is _____



7. For the reaction, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the equilibrium constant $K_P = 5.0$ at 207 ºC. If the partial pressures of SO_2, O_2 and SO_3 are 1.0×10^{-3}, 0.20 and 1.0×10^{-4}, respectively, then the Gibbs free energy of the reaction $\left(\Delta_r G\right)$ in kJ mol^{-1} at 207 ºC is _____ [Given : R = 8.314 J K^{-1} mol^{-1}]

8. In the given list, the total number of compounds that form a clear homogeneous solution on treatment with cold dilute H_2SO_4 is _____
1-propyne
cyclohexanone
cyclohexane
1-propene
propane-1-amine
propoxypropane
tetrahydropyran
ethyl butanoate
pyridine

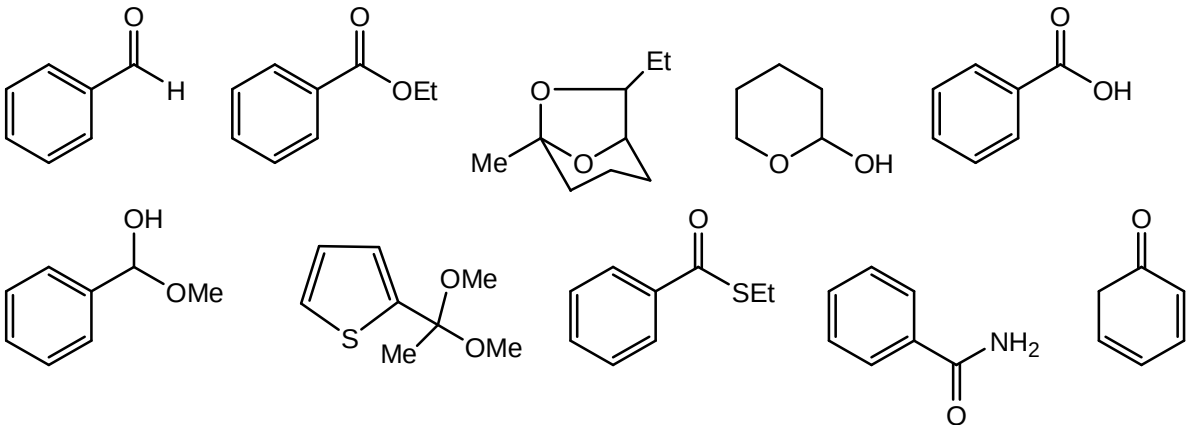
9. Two moles of an ideal gas is expanded isothermally and reversibly from 5 to 1 bar at 298K. The change in the entropy (in JK^{-1}) of the system is _____

10. The pKa values of H_3PO_4 are 2.12, 7.21 and 12.67. The pH of a phosphate buffer containing 0.2M NaH_2PO_4 and 0.1 M Na_2HPO_4 is _____

11. The ionic radii of Cs^+ and Cl^- ions are 181 and 167 pm, respectively. The Born exponents for the He, Ne, Ar, Kr and Xe configuration are 5, 7, 9, 10 and 12 respectively. If the value of $\frac{ANe^2}{4\pi\varepsilon_0}$ is 2.45×10^{-4} Jm, the lattice energy (in kJ mol^{-1}) of CsCl according to Born-Lande equation is _____

12. A 2.5×10^{-4} M solution of a complex exhibits an absorption maximum at 625 nm with an absorbance of 0.90 when measured in a cuvette with a path length of 1.5 cm. The absorbance of 1.5×10^{-3} M solution of the same complex recorded in a cuvette with a path length of 0.2 cm is _____

13. The total number of compounds (shown below) that form phenylhydrazone derivatives under acidic conditions is _____



14. The standard reduction potentials of the Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe couples are 0.77 and –0.44 V respectively. The standard reduction potential (in V) for the Fe^{3+}/Fe couple is _____

15. The number of possible monoalkylated products formed in the Friedel-Crafts reaction of anisole with 2-chloro-3-methylbutane in the presence of anhydrous $AlCl_3$ at 50 °C is _____

16. In an ideal monoatomic gas, the speed of sound is given by $\sqrt{\frac{5RT}{3M}}$. If the speed of sound in argon at 25°C is 1245 km h^{-1}, the root mean square velocity in m s^{-1} is _____

17. A wood specimen containing ^{14}C taken from an ancient palace showed 24 counts in 3 minutes per gram of carbon in a detector. However, a fresh wood showed 52 counts in 2 minutes per gram of carbon. Assuming no background signal in the detector and half life of ^{14}C as 5730 years, the age (in year) of the wood specimen is _____

18. The magnetic field (in Tesla) required for flipping a ^1H nucleus in an NMR spectrometer operating at 400 MHz is _____ [Given : $\gamma = 2.67\times10^8 T^{-1}s^{-1}$, $\pi = 3.14$]

19. For a reaction, the rate constant at 25°C is doubled when the temperature is raised to 45 °C. The activation energy (in kJ mol^{-1}) of the reaction is _____ [Given : ln2 = 0.693]

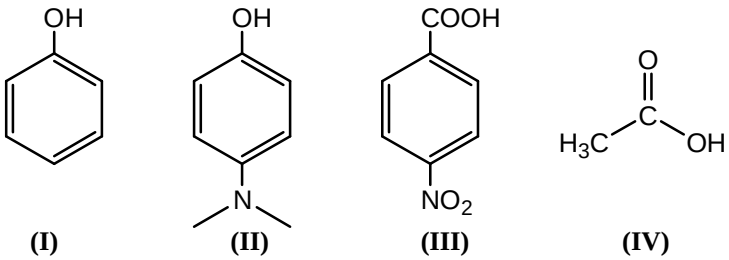
20. When a perfect monolayer of stearic acid is formed at the air-water interface, each molecule of stearic acid (MW = 284, density = 0.94 g cm^{-3}) occupies an area of 20 $Å^2$. The length (in Å) of the molecule is _____

Section-A

Multiple Choice Questions (MCQ)

Q.1 – Q.10 carry ONE mark each.

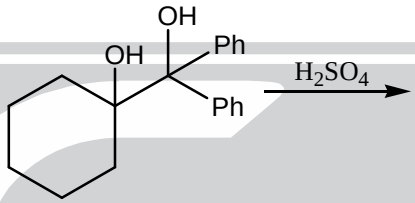
1. The correct order of pKa for the following compounds is

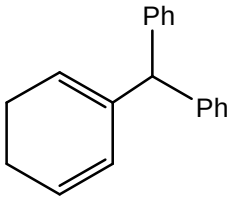


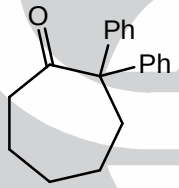
(I) (II) (III) (IV)

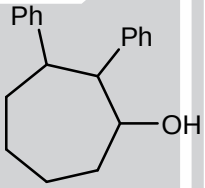
(A) II > I > III > IV (B) II > I > IV > III (C) III > IV > I > II (D) IV > II > I > III

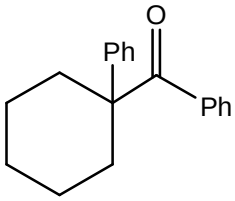
2. The major product formed in the following reaction is



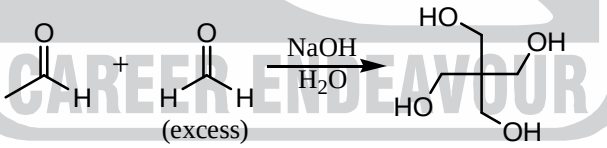
(A)


(B)


(C)


(D)


3. The mechanism of the following transformation involves



(A) Aldol reaction and Cannizzaro reaction

(B) Aldol reaction and Claisen-Schmidt reaction

(C) Knoevenagel condensation and Cannizzaro reaction

(D) Stobbe condensation and Cannizzaro reaction

4. The most basic amino acid among the following is

(A) tyrosine (B) methionine (C) arginine (D) glutamine

5. The crystal field stabilization energy (CFSE) in $[Mn(H_2O)_6]^{2+}$ is

(A) $0\ \Delta_0$ (B) $2.0\ \Delta_0 - 2P$ (C) $0.4\ \Delta_0 - 2P$ (D) $2.0\ \Delta_0$

6. Indicator used in redox titration is

(A) Eriochrome black T (B) Methyl orange (C) Phenolphthalein (D) Methylene blue

7. Among the following, the compound that has the lowest degree of ionic character is

(A) NaCl (B) $MgCl_2$ (C) $AlCl_3$ (D) $CaCl_2$

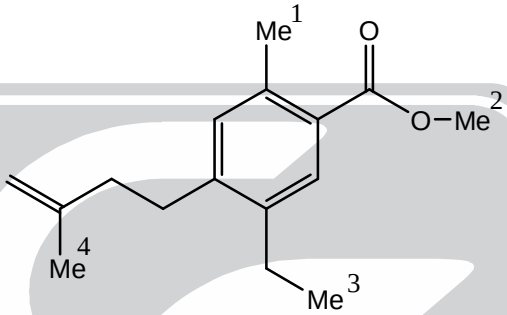
8. The correct order of entropy for various states of CO_2 is
(A) $CO_2(s) > CO_2(l) > CO_2(g)$ (B) $CO_2(l) > CO_2(s) > CO_2(g)$
(C) $CO_2(g) > CO_2(l) > CO_2(s)$ (D) $CO_2(g) > CO_2(s) > CO_2(l)$

9. The coordination numbers of Cs^+ and Cl^- ions in the CsCl structure, respectively, are
(A) 4, 4 (B) 4, 8 (C) 6, 6 (D) 8, 8

10. Determinant of a square matrix is always
(A) a square matrix (B) a column matrix (C) a row matrix (D) a number

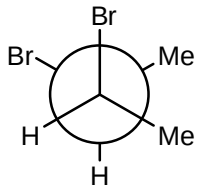
Q.11 – Q.30 carry TWO marks each.

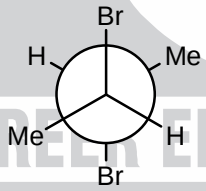
11. The correct order of ^1H NMR chemical shift (δ) values for the labeled methyl groups in the following compound is

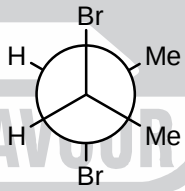


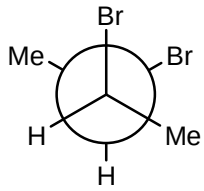
(A) $Me^1 < Me^2 < Me^3 < Me^4$ (B) $Me^3 < Me^4 < Me^1 < Me^2$
(C) $Me^3 < Me^1 < Me^4 < Me^2$ (D) $Me^2 < Me^4 < Me^3 < Me^1$

12. Among the following, the most stable conformation of meso-2, 3-dibromobutane is

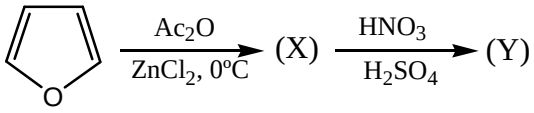
(A) 

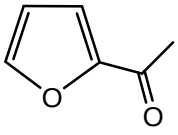
(B) 

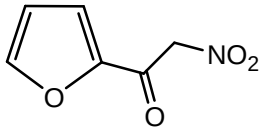
(C) 

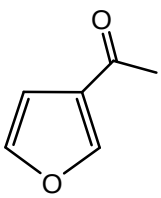
(D) 

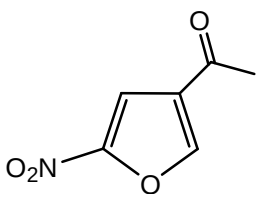
13. The major products X and Y in the following reaction sequence are

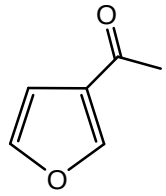
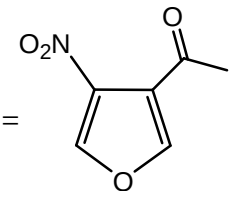


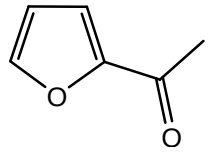
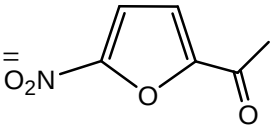
(A) X = 

Y = 

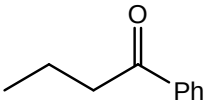
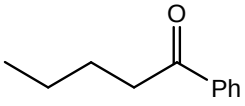
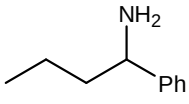
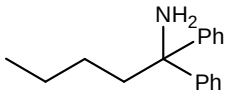
(B) X = 

Y = 

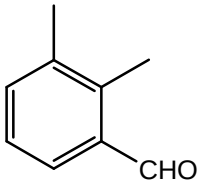
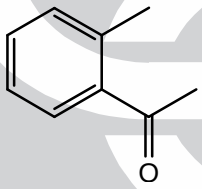
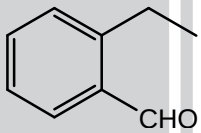
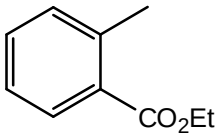
(C) X =  Y = 

(D) X =  Y = 

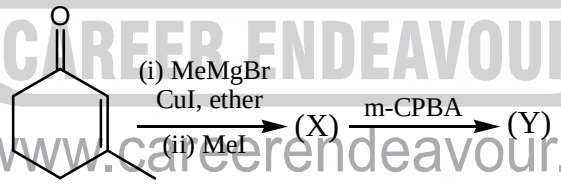
14. The major product formed in the reaction of butanenitrile with phenylmagnesium bromide followed by acidification is

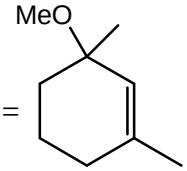
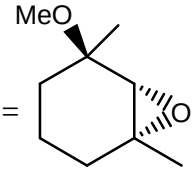
(A)  (B)  (C)  (D) 

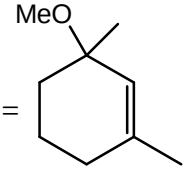
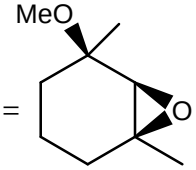
15. An organic compound on reaction with 2, 4-dinitrophenylhydrazine (2, 4-DNP) gives a yellow precipitate. It also gives silver mirror on reaction with ammonical $AgNO_3$. It gives an alcohol and sodium salt of a carboxylic acid on reaction with concentrated NaOH. It yields benzene-1, 2-dicarboxylic acid on heating with alkaline $KMnO_4$. The structure of the compound among the following is

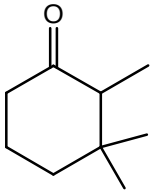
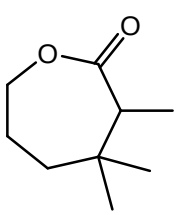
(A)  (B)  (C)  (D) 

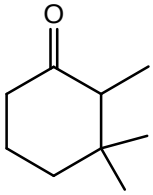
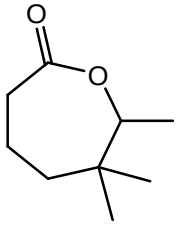
16. The major products X and Y in the following reaction sequence are



(A) X =  Y = 

(B) X =  Y = 

(C) X =  Y = 

(D) X =  Y = 

17. The TRUE statement about $[Cu(H_2O)_6]^{2+}$ is
(A) All Cu-O bond lengths are equal
(B) One Cu-O bond length is shorter than the remaining five
(C) Three Cu-O bond lengths are shorter than the remaining three
(D) Four Cu-O bond lengths are shorter than the remaining two

18. The complexes $\left[Pt(CN)_4\right]^{2-}$ and $\left[NiCl_4\right]^{2-}$, respectively, are
(A) paramagnetic, paramagnetic
(B) diamagnetic, diamagnetic
(C) paramagnetic, diamagnetic
(D) diamagnetic, paramagnetic

19. The value of 'x' in $\left[Cu(CO)_x\right]^{+}$ such that it obeys the 18 electron rule is
(A) 6 (B) 5 (C) 4 (D) 3

20. The correct order of $\nu_{NO}\left(cm^{-1}\right)$ in the following compounds is
(A) $NO^+ > NO > [NiCp(NO)] > [Cr(Cp)_2(NO)_4]$
(B) $[Cr(Cp)_2(NO)_4] > [NiCp(NO)] > NO^+ > NO$
(C) $NO^+ > [Cr(Cp)_2(NO)_4] > NO > [NiCp(NO)]$
(D) $[NiCp(NO)] > NO > [Cr(Cp)_2(NO)_4] > NO^+$

21. The red color of ruby is due to
(A) d-d transition of Cr^{3+} ion in Cr_2O_3 lattice
(B) d-d transition of Cr^{3+} ion in Al_2O_3 lattice.
(C) ligand to metal charge transfer transition
(D) metal to metal charge transfer transition

22. The final products in the reaction of BF_3 with water are
(A) $B(OH)_3$ and OF_2 (B) H_3BO_3 and HBF_4 (C) B_2O_3 and HBF_4 (D) B_2H_6 and HF

23. The correct order of bond angles in BF_3, NH_3, NF_3 and PH_3 is
(A) $BF_3 > NH_3 > NF_3 > PH_3$
(B) $PH_3 > BF_3 > NF_3 > NH_3$
(C) $BF_3 > PH_3 > NH_3 > NF_3$
(D) $NH_3 > NF_3 > BF_3 > PH_3$

24. The maximum of a function $Ae^{-ax^2}\ (A > 0; a > 0)$ is at x =
(A) 0 (B) $+\infty$ (C) $-\infty$ (D) $\frac{1}{\sqrt{a}}$

25. At 298K, 0.1 mol of ammonium acetate and 0.14 mol of acetic acid are dissolved in 1 L of water. The pH of the resulting solution is [Given : pK_a of acetic acid is 4.75]
(A) 4.9 (B) 4.6 (C) 4.3 (D) 2.3

26. An electrochemical cell consists of two half-cell reactions

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$$
$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

The mass of copper (in grams) dissolved on passing 0.5A current for 1 hour is
[Given: atomic mass of Cu is 63.6; F = 96500 C mol^{-1}]
(A) 0.88 (B) 1.18 (C) 0.29 (D) 0.59

27. For a zero order reaction, the half-life depends on the initial concentration $[C_0]$ of the reactant as
(A) $[C_0]$ (B) $[C_0]^0$ (C) $[C_0]^{-1}$ (D) $[C_0]^{1/2}$

28. The effective nuclear charge of helium atom is 1.7. The first ionization energy of helium atom in eV is
(A) 13.6 (B) 23.1 (C) 39.3 (D) 27.2

29. The relationship between the van der Waals 'b' coefficient of N_2 and O_2 is
(A) $b(N_2) = b(O_2) = 0$ (B) $b(N_2) = b(O_2) \neq 0$
(C) $b(N_2) > b(O_2)$ (D) $b(N_2) < b(O_2)$

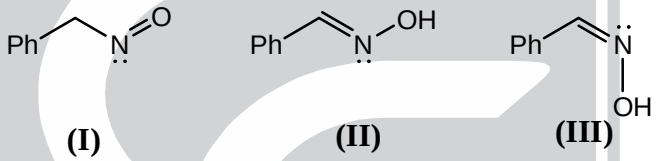
30. From the kinetic theory of gases, the ratio of most probable speed (C_{mp}) to root mean square speed (C_{rms}) is
(A) $\sqrt{3}$ (B) $\sqrt{2}/\sqrt{3}$ (C) $\sqrt{3}/\sqrt{2}$ (D) $3/\sqrt{2}$

Section-B

Multiple Select Questions (MSQ)

Q.31 – Q.40 carry TWO marks each.

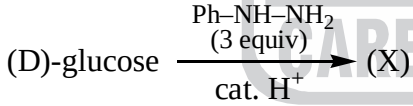
31. The correct statement(s) about the following species is(are)



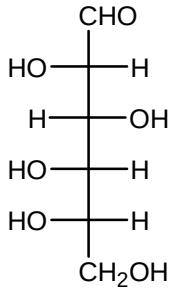
(I) **(II)** **(III)**

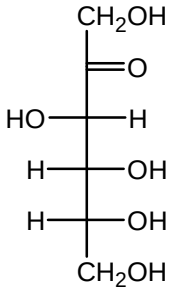
(A) I and II are resonance structures
(B) II and III are resonance structures
(C) II and III are diastereomers
(D) III is a tautomer of I

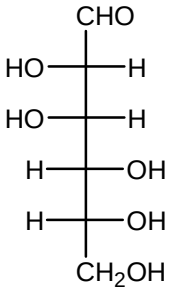
32. Consider the following reaction:

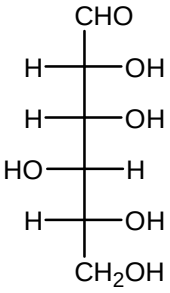


Among the following, the compound(s) whose osazone derivatives(s) will have the same melting point as that of X is(are)

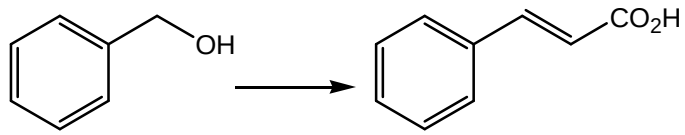
(A)


(B)


(C)


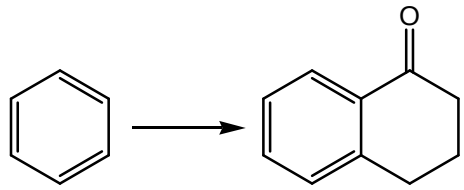
(D)


33. The appropriate reagents required for carrying out the following transformation are



(A) (i) PCC, CH_2Cl_2; (ii) $Ph_3P{=}CHCO_2Et$; (iii) aq. NaOH, heat, then acidify
(B) (i) CrO_3, H_2SO_4, aq. acetone (ii) Ac_2O, NaOAc
(C) (i) MnO_2; (ii) $CH_2(CO_2H)_2$, piperidine, pyridine
(D) (i) PCC; CH_2Cl_2; (ii) $BrCH_2CO_2C(CH_3)_3$, Zn (iii) H_3O^+, heat

34. The appropriate reagents required for carrying out the following transformation are



(A) (i) succinic anhydride, $AlCl_3$; (ii) Zn/Hg, HCl; (iii) polyphosphoric acid
(B) (i) maleic anhydride, $AlCl_3$; (ii) $H_2N\text{-}NH_2$, KOH; (iii) H_2SO_4
(C) (i) succinic anhydride, $FeCl_3$; (ii) $LiAlH_4$; (iii) H_2SO_4
(D) (i) phthalic anhyride, $F_3B.OEt_2$; (ii) $HS(CH_2)_2SH$, H^+; (iii) Raney Ni; (iv) polyphosphoric acid

35. The protein(s) that belong to the class of blue copper proteins is(are)
(A) ceruloplasmin (B) superoxide dismutase (C) hemocyanin (D) azurin

36. The ion(s) that exhibit only charge transfer bands in the absorption spectra (UV-visible region) is/are
(A) $\left[Cr\left(C_2O_4\right)_3\right]^{3-}$ (B) $\left[CrO_4\right]^{2-}$ (C) $\left[ReO_4\right]^{-}$ (D) $\left[NiO_2\right]^{2-}$

37. The type(s) of interaction(s) that hold layers of graphite together is(are)
(A) $\pi-\pi$ stacking (B) van der Waals (C) hydrogen bonding (D) Coulombic

38. TRUE statement(s) about Langmuir isotherm is(are)
(A) valid for monolayer coverage
(B) all adsorption sites are equivalent
(C) there is dynamic equilibrium between free gas and adsorbed gas
(D) adsorption probability is independent of occupancy at the neighboring sites

39. The $3p_z$ orbital has
(A) one radial node (B) two radial nodes (C) one angular node (D) two angular nodes

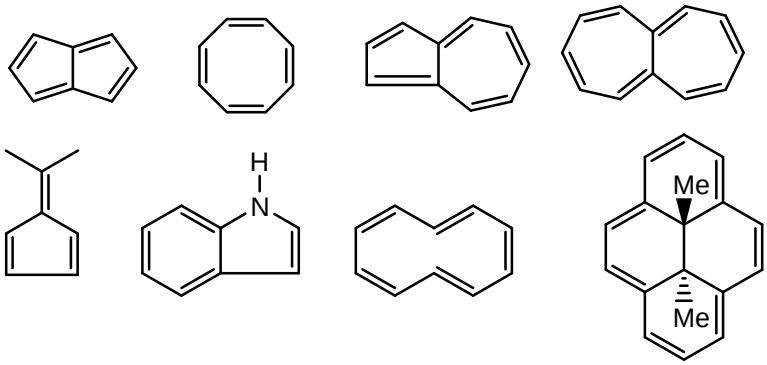
40. The diatomic molecule(s) that has (have) two π-type bonds is(are)
(A) B_2 (B) C_2 (C) N_2 (D) O_2

Section-C

Numerical Answer Type (NAT)

Q.41 – Q.50 carry ONE mark each.

41. Among the following, the number of molecules that are aromatic is



42. The number of all possible isomers for the molecular formula C_6H_{14} is _____

43. Hydrolysis of 15.45g of benzonitrile produced 10.98 g of benzoic acid. The percentage yield of acid formed is _____

44. Acetic acid content in commercial vinegar was analyzed by titrating against 1.5 M NaOH solution. A 20 mL vinegar sample required 18 mL of titrant to give endpoint. The concentration of acetic acid in the vinegar (in mol L^{-1}) is _____

45. The bond order of Be_2 molecule is _____

46. The number of P-H bonds in hypophosphorus acid is _____

47. The isotope $^{217}_{84}Po$ undergoes one alpha and one beta particle emission sequentially to form an isotope "X". The number of neutrons in "X" is _____

48. In a diffraction experiment with X-rays of wavelength 1.54Å, a diffraction line corresponding to $2\theta = 20.8^{o}$ is observed. The inter-planar separation in Å is _____

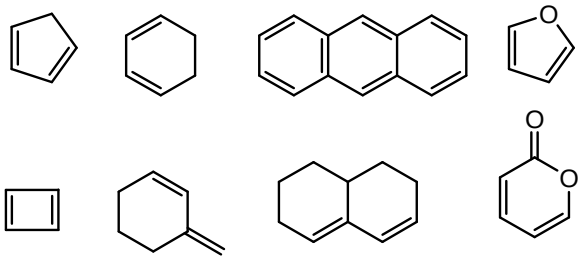
49. The potential energy of interaction between two ions in an ionic compound is given by $U = 1389.4\left[\frac{Z_1Z_2}{r/Å}\right]$ kJ mol^{-1}. Assuming that $CaCl_2$ is linear molecule of length 5.6Å, the potential energy for $CaCl_2$ molecule in kJ mol^{-1} is _____

50. The enthalpy of formation for $CH_4(g)$, C(g) and H(g) are –75, 717 and 218 kJ mol^{-1}, respectively. The enthalpy of the C-H bond in kJ mol^{-1} is ._____

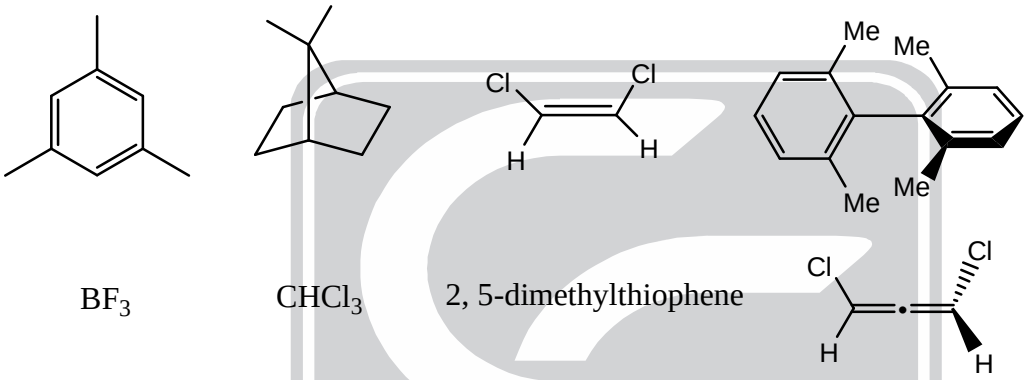
Q.51 – Q.60 carry TWO marks each.

51. Specific rotation of the (R)-enantiomer of a chiral compound is 48°. The specific rotation of a sample of this compound which contains 25% of (S)-enantiomer is _____

52. Among the following, the number of compounds, which can participates as 'diene' component in a Diels-Alder reaction is _____



53. Among the following, the number of molecules that possess C_2 axis of symmetry is _____



BF_3 $CHCl_3$ 2, 5-dimethylthiophene

54. Effective nuclear charge for 3d electron in vanadium (atomic number = 23) according to Slater's rule is _____

55. The total number of isomers possible for the molecule $\left[Co(NH_3)_4 Cl(NO_2)\right]^+$ is _____

56. The bond angle in PBr_3 is 101°. The percent **'s'** character of the central atom is _____

57. $Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow 2NO_2(g) + Cu^{2+}(aq) + 2H_2O(\ell)$

In the above reaction at 1 atm and 298K, if 6.36 g of copper is used. Assuming ideal gas behaviour, the volume of NO_2 produced in liters is _____

[Given : atomic mass of Cu is 63.6; R = 0.0821 L atm K^{-1} mol^{-1}]

58. The ΔH^0 for the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ at 400K in kJ mol^{-1} is _____

Given at 298K :

	ΔH_f^0	C_p^0
	kJ mol^{-1}	J $mol^{-1}K^{-1}$
O_2	0	29.4
CO	–110	29.1
CO_2	–394	37.1

59. The rate constants for a reaction at 300 and 350 K are 8 and 160 L mol^{-1} s^{-1}, respectively. The activation energy of the reaction in kJ mol^{-1} is _____
[Given : R = 8.314 JK^{-1} mol^{-1}].

60. A 10 L flask containing 10.8 g of N_2O_5 is heated to 373K, which leads to its decomposition according to the equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. If the final pressure in the flask is 0.5 atm, then the partial pressure of O_2(g) in atm is _____
[Given : R = 0.0821 L atm K^{-1} mol^{-1}]

***** END OF THE QUESTION PAPER *****

PAPER : IIT-JAM 2017

CHEMISTRY-CY

1. **Section-A contains 30 Multiple Choice Questions (MCQ). Each question has 4 choices (a), (b), (c) and (d), for its answer, out of which ONLY ONE is correct. From Q.1 to Q.10 carries 1 Marks and Q.11 to Q.30 carries 2 Marks each.**
2. **Section-B contains 10 Multiple Select Questions(MSQ). Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE or MORE than ONE is/are correct. For each correct answer you will be awarded 2 marks.**
3. **Section-C contains 20 Numerical Answer Type (NAT) questions. From Q.41 to Q.50 carries 1 Mark each and Q.51 to Q.60 carries 2 Marks each. For each NAT type question, the value of answer in between 0 to 9.**
4. **In all sections, questions not attempted will result in zero mark. In Section–A (MCQ), wrong answer will result in negative marks. For all 1 mark questions, 1/3 marks will be deducted for each wrong answer. For all 2 marks questions, 2/3 marks will be deducted for each wrong answer. In Section–B (MSQ),there is no negative and no partial marking provisions. There is no negative marking in Section–C (NAT) as well.**

SECTION-A

Multiple Choice Questions (MCQ)

Q.1 – Q.10 carry ONE mark each.

1. The correct order of the boiling points of the compounds is

(A) $CH_4 > SiH_4 > SnH_4 > GeH_4$ (B) $SiH_4 > CH_4 > GeH_4 > SnH_4$

(C) $SnH_4 > GeH_4 > CH_4 > SiH_4$ (D) $SnH_4 > GeH_4 > SiH_4 > CH_4$

2. In the following Latimer diagram, the species that undergoes disproportionation reaction is

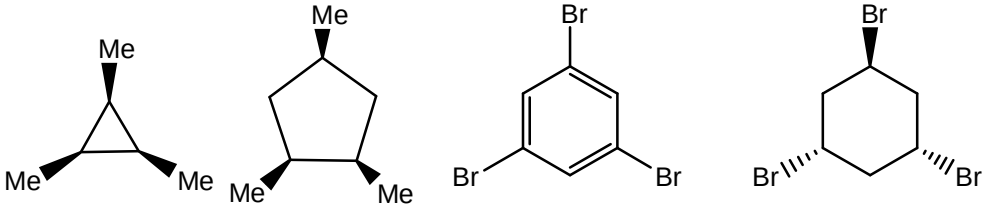
$$MnO_4^- \xrightarrow{+0.56} MnO_4^{2-} \xrightarrow{+0.27} MnO_4^{3-} \xrightarrow{+0.93} MnO_2 \xrightarrow{+0.15} Mn_2O_3 \xrightarrow{-0.25} Mn(OH)_2 \xrightarrow{-1.56} Mn$$

(A) MnO_4^{2-} (B) MnO_4^{3-} (C) Mn_2O_3 (D) $Mn(OH)_2$

3. A yellow precipitate is formed upon addition of aqueous $AgNO_3$ to a solution of

(A) phosphite (B) pyrophosphate (C) metaphosphate (D) orthophosphate

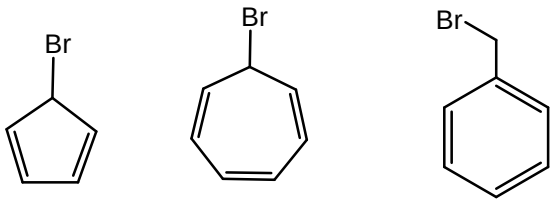
4. The compounds having C_3-axis of symmetry are



(I) **(II)** **(III)** **(IV)**

(A) I, III and IV (B) I, II and III (C) I and III (D) III and IV

5. The correct order of rate of solvolysis for the following compounds is



(I) **(II)** **(III)**

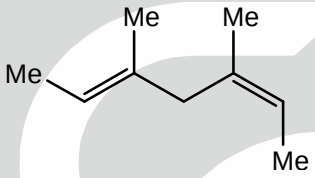
(A) III > II > I (B) II > I > III (C) III > I > II (D) II > III > I

6. In the following sequence of reactions, the overall yield (%) of O is

$$L \xrightarrow{92\%\ \text{yield}} M \xrightarrow{78\%\ \text{yield}} N \xrightarrow{85\%\ \text{yield}} O$$

(A) 61 (B) 85 (C) 74 (D) 68

7. Catalytic hydrogenation of the following compound produces saturated hydrocarbon(s). The number of stereoisomer(s) formed is



(A) 1 (B) 2 (C) 3 (D) 4

8. The number of normal modes of vibration in naphthalene is

(A) 55 (B) 54 (C) 48 (D) 49

9. The number of degrees of freedom of liquid water in equilibrium with ice is

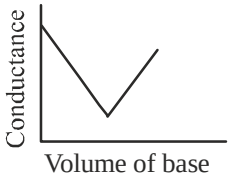
(A) 0 (B) 1 (C) 2 (D) 3

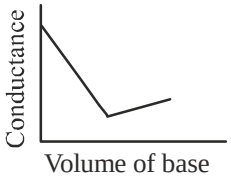
10. A straight line having a slope of $-\frac{\Delta U^0}{R}$ is obtained in a plot between

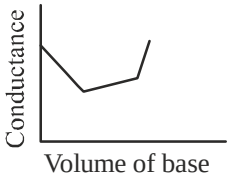
(A) $\ln(K_p)$ versus T (B) $\ln(K_c)$ versus T (C) $\ln(K_p)$ versus 1/T (D) $\ln(K_c)$ versus 1/T

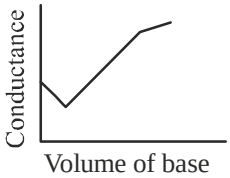
Q.11 – Q.30 carry TWO marks each.

11. In a typical conductometric titration of a strong acid with a weak base, the curve resembles

(A) 

(B) 

(C) 

(D) 

12. The coordination number of Al in crystalline $AlCl_3$ and liquid $AlCl_3$, respectively, is

(A) 4 and 4 (B) 6 and 6 (C) 6 and 4 (D) 3 and 6

13. The homogeneous catalyst used in water-gas shift reaction is

(A) $PdCl_2$ (B) Cr_2O_3

(C) $[RhCl(PPh_3)_3]$ (D) $[RuCl_2(bipyridyl)_2]$

14. Nitrosyl ligand binds to d-metal atoms in linear and bent fashion and behaves, respectively, as
(A) NO^+ anad NO^+ (B) NO^+ and NO^- (C) NO^- and NO^- (D) NO^- and NO^+

15. The metal ion (M^{2+}) in the following reaction is

$$M^{2+} + S^{2-} \longrightarrow \text{Black precipitate} \xrightarrow{\text{hot conc. } HNO_3} \text{White precipitate}$$

(A) Mn^{2+} (B) Fe^{2+} (C) Cd^{2+} (D) Cu^{2+}

16. The correct order of wavelength of absorption (λ_{max}) of the Cr-complexes is (en = ethylenediamine)

(A) $[CrF_6]^{3-} > [Cr(H_2O)_6]^{3+} > [Cr(en)_3]^{3+} > [Cr(CN)_6]^{3-}$

(B) $[Cr(H_2O)_6]^{3+} > [CrF_6]^{3-} > [Cr(en)_3]^{3+} > [Cr(CN)_6]^{3-}$

(C) $[Cr(CN)_6]^{3-} > [Cr(en)_3]^{3+} > [Cr(H_2O)_6]^{3+} > [CrF_6]^{3-}$

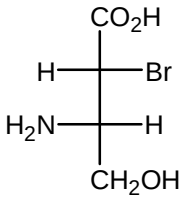
(D) $[Cr(en)_3]^{3+} > [Cr(CN)_6]^{3-} > [Cr(H_2O)_6]^{3+} > [CrF_6]^{3-}$

17. The correct order of enthalpy of the hydration for the transition metal ions is

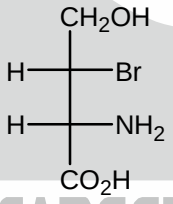
(A) $Cr^{3+} > Mn^{2+} > Co^{2+} > Ni^{2+}$ (B) $Ni^{2+} > Co^{2+} > Mn^{2+} > Cr^{2+}$

(C) $Ni^{2+} > Co^{2+} > Cr^{2+} > Mn^{2+}$ (D) $Cr^{2+} > Mn^{2+} > Ni^{2+} > Co^{2+}$

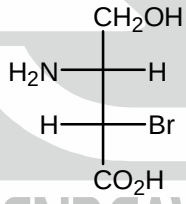
18. Among the following compounds, the pair of enantiomers is



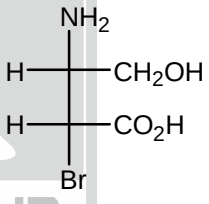
(I)



(II)



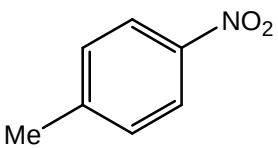
(III)



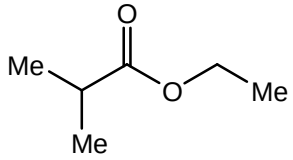
(IV)

(A) I and IV (B) I and III (C) II and III (D) III and IV

19. The number of proton NMR signals for the compounds P and Q, respectively, is



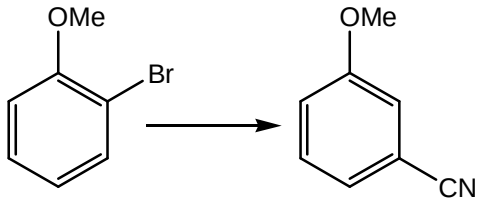
(P)



(Q)

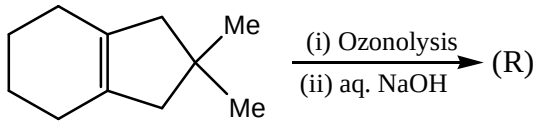
(A) 3 and 4 (B) 3 and 5 (C) 4 and 3 (D) 5 and 4

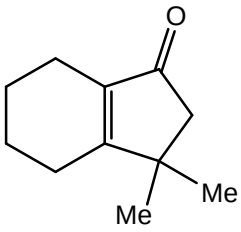
20. The correct set of reagents for the following conversion is

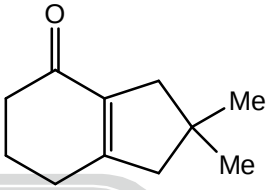


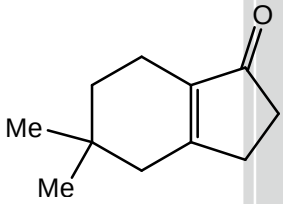
(A) (i) $NaNH_2$/liq. NH_3; (ii) $NaNO_2$/dil, HCl; (iii) CuCN, heat
(B) (i) HNO_3/H_2SO_4; (ii) Zn/HCl; (iii) $NaNO_2$/dil. HCl; (iv) CuCN, heat
(C) (i) Mg/ether, H_3O^+; (ii) $(EtO)_2CO$; (iii) NH_4OH; (iv) PCl_5
(D) (i) Mg/ether, H_3O^+; (ii) HNO_3/H_2SO_4; (iii) $NaNO_2$/dil. HCl; (iv) CuCN, heat

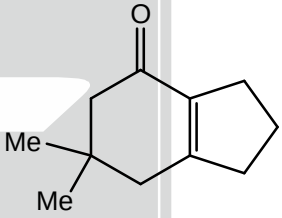
21. The product R in the following reaction is



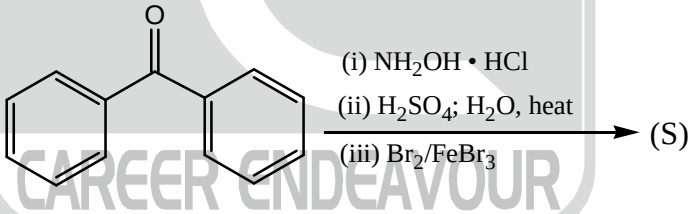
(A)


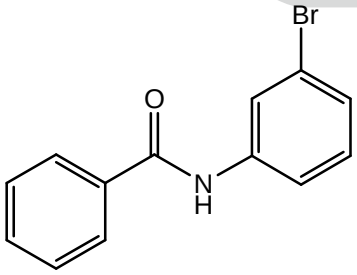
(B)


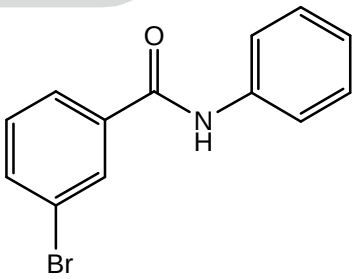
(C)


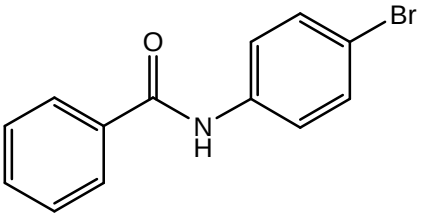
(D)


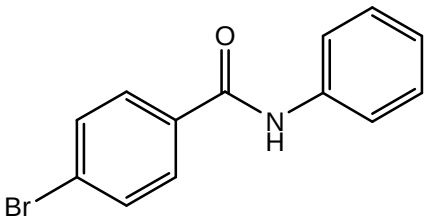
22. The major product S of the following reaction is



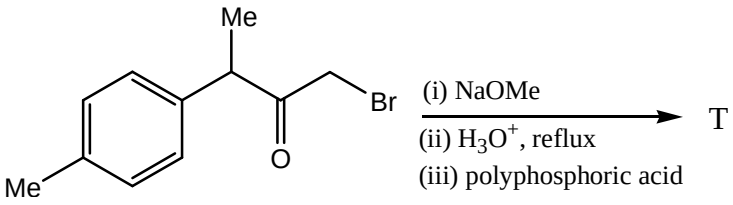
(A)


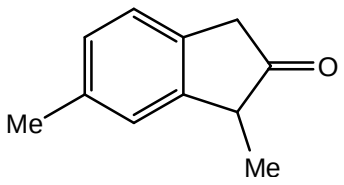
(B)


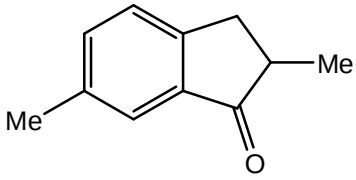
(C)


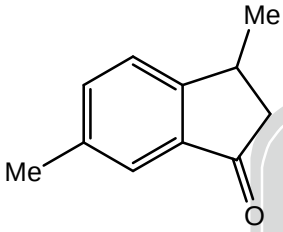
(D)


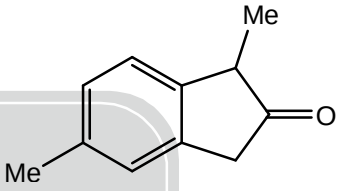
23. In the following reaction, the major product T is



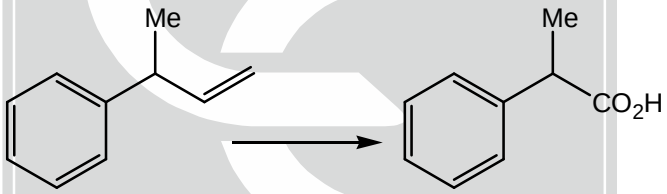
(A) 

(B) 

(C) 

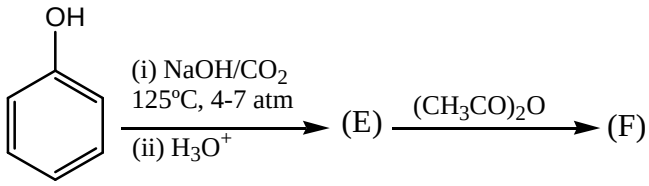
(D) 

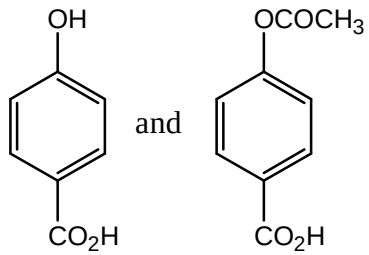
24. The following conversion is carried out using

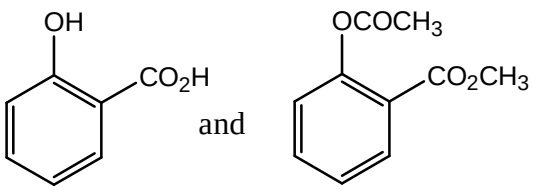


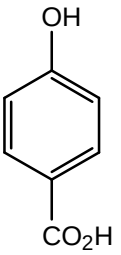
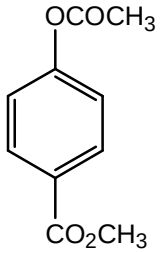
(A) hydroboration-oxidation followed by Jones oxidation
(B) Wacker oxidation followed by haloform reaction
(C) oxymercuration-demercuration followed by Jones oxidation
(D) ozonolysis followed by haloform reaction

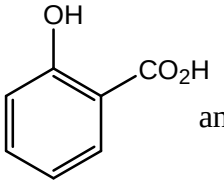
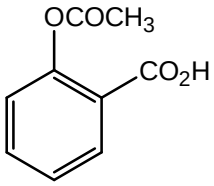
25. In the following reactions, the major product E and F, respectively, are



(A) 

(B) 

(C)  and 

(D)  and 

26. $\frac{dy}{dx} = -\frac{y}{x}$ is a differential equation for a/an

(A) circle (B) ellipse (C) bell-shaped curve (D) hyperbola

27. Value of the given determinant is

$$\begin{bmatrix} 1 & 3 & 0 \\ 2 & 6 & 4 \\ -1 & 0 & 2 \end{bmatrix}$$

(A) –12 (B) 0 (C) 6 (D) 12

28. Ionisation energy of the hydrogen atom in ground state is 13.6 eV. The energy released (in eV) for third member of Balmer series is

(A) 13.056 (B) 2.856 (C) 0.967 (D) 0.306

29. For a first order reaction $A(g) \rightarrow 2B(g) + C(g)$, the rate constant in terms of initial pressure (p_0) and pressure at time $t(p_t)$, is given by

(A) $\frac{1}{t}\ell n\frac{p_0}{p_t - p_0}$ (B) $\frac{1}{t}\ell n\frac{2p_0}{3p_0 - p_t}$ (C) $\frac{1}{t}\ell n\frac{3p_0}{p_t - p_0}$ (D) $\frac{1}{t}\ell n\frac{3p_0}{3p_t - p_0}$

30. For a particle in one-dimensional box of length L with potential energy $V(x) = 0$ for $L > x > 0$ and $V(x) = \infty$ for $x \geq L$ and $x \leq 0$, an acceptable wave function consistent with the boundary conditions is (*A*, *B*, *C* and *D* are constants)

(A) $A\cos\left(\frac{n\pi x}{L}\right)$ (B) $B\left(x + x^2\right)$ (C) $Cx^3(x - L)$ (D) $\frac{D}{\sin\left(\frac{n\pi x}{L}\right)}$

SECTION-B

Multiple Select Questions (MSQ)

Q.31 – Q.40 carry TWO marks each.

31. The 'heme' containing protein(s) is/are
(A) cytochrome C (B) hemocyanin (C) hemerythrin (D) myoglobin

32. Among the following, the species having see-saw shape is/are
(A) SF_4 (B) XeF_4 (C) ClF_4^+ (D) ClF_4^-

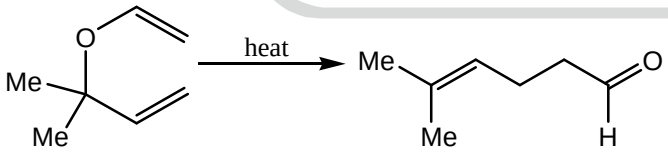
33. The indicator(s) appropriate for the determination of end point in the titration of a weak acid with a strong base is/are
(A) phenolphthalein (B) thymol blue (C) bromophenol blue (D) methyl orange

34. Jahn-Teller distortion is/are observed in octahedral complexes with d-electron configuration of
(A) d^5-high spin (B) d^5-low spin (C) d^6-high spin (D) d^6-low spin

35. Among the following, the correct statement(s) is/are
(A) Guanine is a purine nucleobase
(B) Glycine and proline are achiral amino acids
(C) DNA contains glycosidic bonds and pentose sugars
(D) Sucrose is a non-reducing sugar

36. The INCORRECT statement(s) among the following is/are
(A) $[4\pi+2\pi]$ cycloaddition reactions are carried out in presence of light
(B) $[2\pi+2\pi]$ cycloaddition reaction between a keto group and an alkene is photochemically allowed
(C) $[4\pi+2\pi]$ cycloaddition reactions are thermally allowed
(D) Transoid dienes undergo Diels-Alder reactions

37. The following conversion(s) is/are example(s) of



(A) oxy-Cope rearrangement (B) sigmatropic rearrangement
(C) Claisen rearrangement (D) pericyclic reaction

38. IR active molecules(s) is/are
(A) CO_2 (B) CS_2 (C) OCS (D) N_2

39. Intensive variable(s) is/are
(A) temperature (B) Volume (C) Pressure (D) Density

40. Wave nature of electromagnetic radiation is observed in
(A) diffraction (B) interference
(C) photoelectric effect (D) Compton scattering

SECTION-C

Numerical Answer Type (NAT)

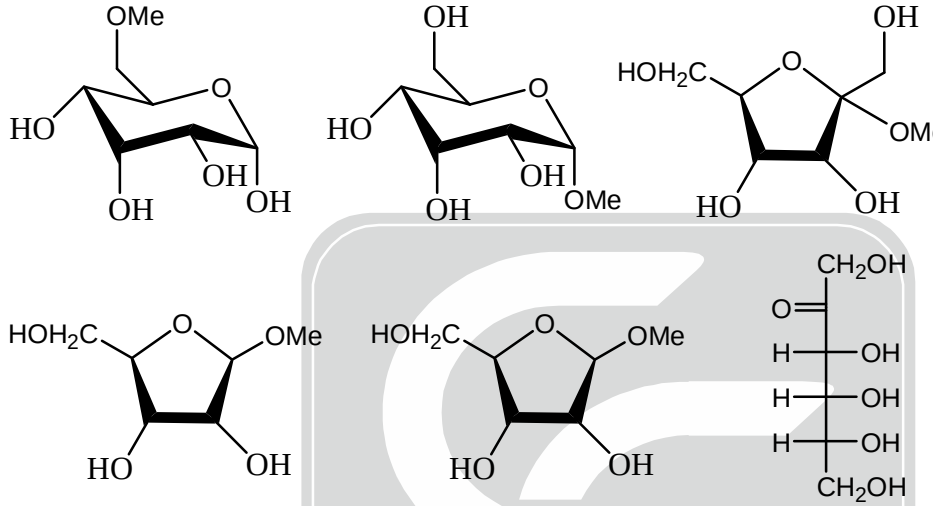
Q.41 – Q.50 carry ONE mark each.

41. The number of isomeric structures of di-substituted borazine $\left[B_3N_3H_4X_2\right]$ is _____

42. The number of S-S bond(s) in tetrathionate ion is _____

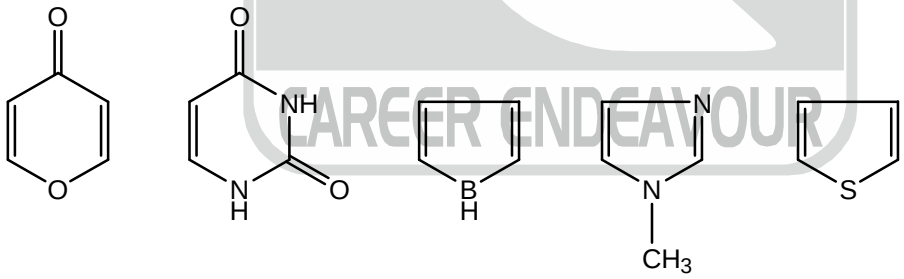
43. The number of unpaired electron(s) in K_2NiF_6 is _____

44. The number of reducing sugars among the following is _____



45. The maximum number of dipeptides that could be obtained by reaction of phenylalanine with leucine is _____

46. Among the following, the number of aromatic compound(s) is_____



47. At an operating frequency of 350 MHz, the shift (in Hz) of resonance from TMS (tetramethylsilane) of a proton with chemical shift of 2 ppm is _____

48. At 298K and 1 atm, the molar enthalpies of combustion of cyclopropane and propene are –2091 kJ mol^{-1} and –2058 kJ mol^{-1}, respectively. The enthalpy change (in kJ mol^{-1}) for the conversion of one mole of propene to one mole of cyclopropane is _____

49. For a cell reaction, $Pb(s)+Hg_2Cl_2(s)\rightarrow PbCl_2(s)+2Hg(\ell)$, $\left(\frac{\partial E^0}{\partial T}\right)_P$ is 1.45×10^{-4} VK^{-1}. The entropy change (in J $mol^{-1}K^{-1}$) for the reaction is _____

50. For a reaction $2A+B\rightarrow C+D$, if rate of consumption of A is 0.1 mol L^{-1} s^{-1}, the rate of production of C (in mol $L^{-1}s^{-1}$) is _____

Q.51 – Q.60 carry TWO marks each.

51. The standard reduction potentials of Ce^{4+}/Ce^{3+} and Fe^{3+}/Fe^{2+} are 1.44 and 0.77V, respectively. The $\log_{10} K$ (K is the equilibrium constant) value for the following reaction is _____ (Final answer should be rounded off to two decimal places)

$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

[Given : RT/F = 0.0257 V]

52. A radioactive element undergoes 80% radiaoctive decay in 300 min. The half-life for this species in minutes is _____

53. Silver crystallizes in a face-centered cubic lattice. The lattice parameter of silver (in picometer) is _____
[**Given :** Avogadro's number = 6.023×10^{23} mol^{-1}, molar mass of silver = 107.87 g mol^{-1} and density of crystal = 10.5 g cm^{-3}]

54. The amount of bromine (atomic wt. = 80) required (in gram) for the estimation of 42.3 g of phenol (molecular wt. = 94 g mol^{-1}) is _____

55. The total number of pair of enantiomeric possible with molecular formula $C_5H_{12}O$ is _____

56. In 200 g of water, 0.01 mole of NaCl and 0.02 mole of sucrose are dissolved. Assuming solution to be ideal, the depression in freezing point of water (in ºC) will be _____
(final answer should be rounded off to two decimal places)

[Given : $K_f\left(H_2O\right) = 1.86$ K kg mol^{-1}**]**

57. The absorption of a gas follows the Langmuir isotherm with K = 1.25 kPa^{-1} at 25ºC. The pressure (in Pa) at which surface coverage is 0.2 is _____

58. The separation of 123 planes (in nm) in an orthorhombic cell with a = 0.25 nm and b = 0.5 nm and c = 0.75 nm is _____
(final answer should be rounded off two decimal places)

59. A vessel contains a mixture of H_2 and N_2 gas. The density of this gas mixture is 0.2 g L^{-1} at 300K and 1 atm. Assuming that both the gases behave ideally, the mole fraction of N_2 (g) in the vessel is _____
(Final answer should be rounded off to two decimal places)
[**Given :** R = 0.082 L atm mol^{-1} K^{-1}, atomic wt. of hydrogen = 1.0 and atomic wt. of nitrogen = 14.0]

60. Consider an isothermal reversible compression of one mole of an ideal gas in which the pressure of the system is increased from 5 atm to 30 atm at 300K. The entropy change of the surroundings (in J K^{-1}) is _____ (final answer should be rounded off to two decimal places)
[**Given** : R = 8.314 J mol^{-1} K^{-1}]

PAPER : IIT-JAM 2018

CHEMISTRY-CY

1. **Section-A contains 30 Multiple Choice Questions (MCQ). Each question has 4 choices (a), (b), (c) and (d), for its answer, out of which ONLY ONE is correct. From Q.1 to Q.10 carries 1 Marks and Q.11 to Q.30 carries 2 Marks each.**
2. **Section-B contains 10 Multiple Select Questions(MSQ). Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE or MORE than ONE is/are correct. For each correct answer you will be awarded 2 marks.**
3. **Section-C contains 20 Numerical Answer Type (NAT) questions. From Q.1 to Q.10 carries 1 Mark each and Q.11 to Q.20 carries 2 Marks each. For each NAT type question, the value of answer in between 0 to 9.**
4. **In all sections, questions not attempted will result in zero mark. In Section–A (MCQ), wrong answer will result in negative marks. For all 1 mark questions, 1/3 marks will be deducted for each wrong answer. For all 2 marks questions, 2/3 marks will be deducted for each wrong answer. In Section–B (MSQ),there is no negative and no partial marking provisions. There is no negative marking in Section–C (NAT) as well.**

SECTION-A

Multiple Choice Questions (MCQ)

Q.1 – Q.10 carry ONE mark each.

1. The number of crystal systems and the number of Bravais lattices are, respectively

   (A) 14 and 7 (B) 7 and 32 (C) 32 and 14 (D) 7 and 14

2. NaF, KF, MgO and CaO are crystalline solids. They have NaCl structure. Their lattice energies vary in the order

   (A) NaF < KF < MgO < CaO (B) KF < NaF < CaO < MgO

   (C) MgO < CaO < NaF < KF (D) CaO < MgO < KF < NaF

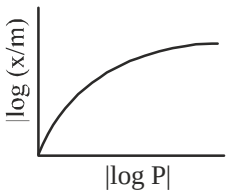
3. On hydrolysis, aluminium carbide produces

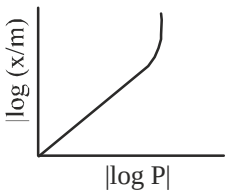
   (A) CH_4 (b) C_2H_6 (C) C_2H_4 (D) C_2H_2

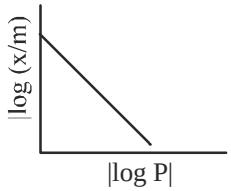
4. The value of integral $\int_{-2}^{+2} x\, e^{-2x^2}\, dx$ is

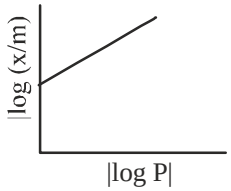
   (a) 0 (b) $\frac{1}{2}$ (c) 1 (d) 2

5. For adsoption of a gas on a solid surface, the plot that represents Freundlich isotherm is (x = mass of gas, M = mass of adsorbent, P = pressure)

   (A) 

   (B) 

(C) 

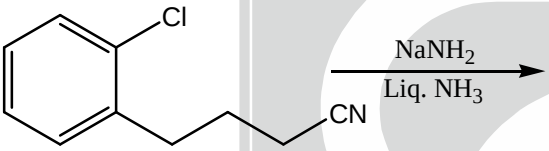
(D) 

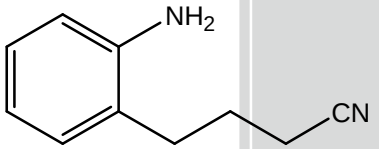
6. The C-2 epimer of D-glucose is
(A) D-Mannose (B) D-Fructose (C) D-Galactose (D) D-Gulose

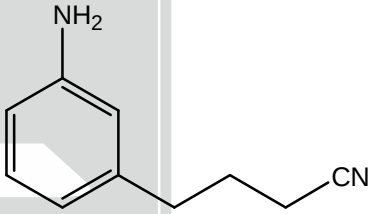
7. Carbonic anhydrase is an example of
(A) Hydrolysis enzyme (B) Redox enzyme
(C) O_2 transport protein (D) Heme protein

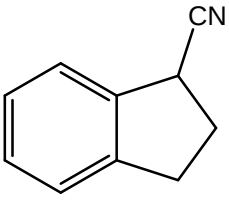
8. The compound that contains the most acidic hydrogen is
(A) $H_2C=CH_2$ (B) $HC\equiv CH$ (C) $H_2C=C=CH_2$ (D) H_3C-CH_3

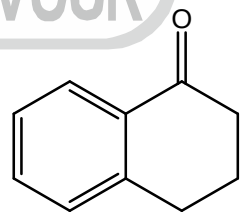
9. The major product formed in the following reaction is



(A) 

(B) 

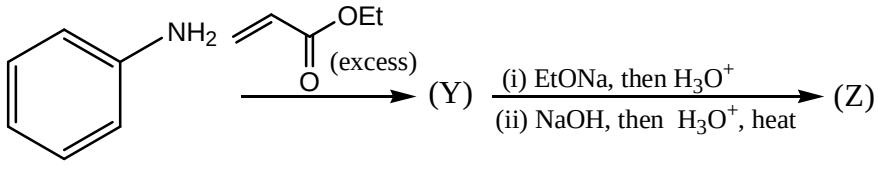
(C) 

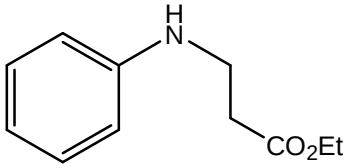
(D) 

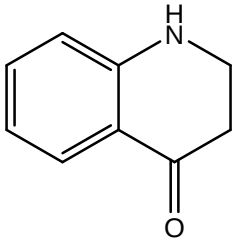
10. The **CORRECT** order of melting points of group 15 trifluorides is
(A) $PF_3 < AsF_3 < SbF_3 < BiF_3$ (B) $BiF_3 < SbF_3 < PF_3 < AsF_3$
(C) $PF_3 < SbF_3 < AsF_3 < BiF_3$ (D) $BiF_3 < AsF_3 < SbF_3 < PF_3$

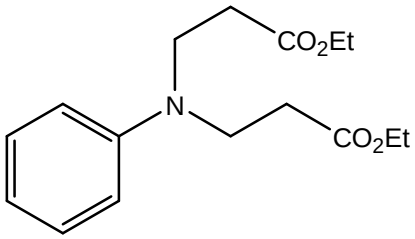
Q.11 – Q.30 carry TWO marks each.

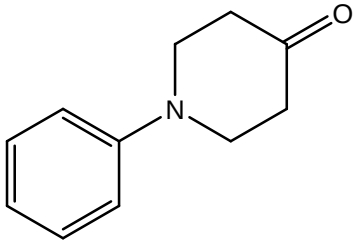
11. The major products Y and Z in the following reaction sequence are

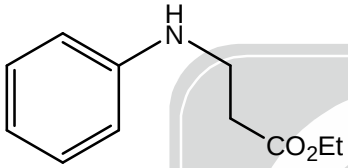


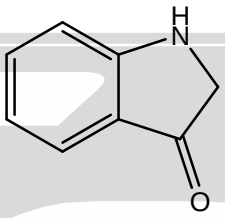
(A) (Y) = 

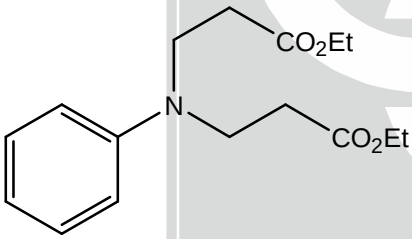
(Z) = 

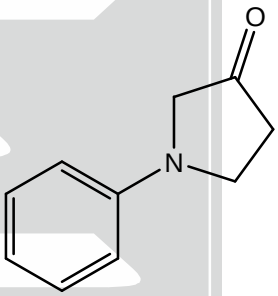
(B) (Y) = 

(Z) = 

(C) (Y) = 

(Z) = 

(D) (Y) = 

(Z) = 

12. The behavior of Cl_2 is closest to ideal gas behavior at
(A) 100ºC and 10.0 atm (B) 0ºC and 0.50 atm
(C) 200 ºC and 0.50 atm (D) –100ºC and 10.0 atm

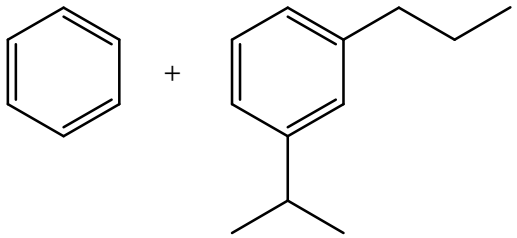
13. With respect to periodic properties, the CORRECT statement is
(a) Electron affinity order is F > O > Cl
(B) First ionisation energy order is Al > Mg > K
(C) Atomic radius order is N > P > As
(D) Ionic radius order is $K^+ > Ca^{2+} > Mg^{2+}$

14. With reference to the variation of molar conductivity (Λ_m) with concentration for a strong electrolyte in an aqueous solution, the CORRECT statement is
(A) The asymmetry effect contributes to decrease Λ_m whereas the electrophoretic effect contributes to increase Λ_m
(B) The asymmetry effect contributes to increase Λ_m whereas the electrophoretic effect contributes to decrease Λ_m
(C) Both asymmetry effect and electrophoretic effect contribute to decrease Λ_m
(D) Both asymmetry effect and electrophoretic effect contribute to increase Λ_m

15. A vector $\vec{A} = \vec{i} + x\vec{j} + 6\vec{k}$ -is rotated through an angle and is also doubled in magnitude resulting in $\vec{B} = 4\vec{i} + (4x-2)\vec{j} + 2\vec{k}$. An acceptable value of x is

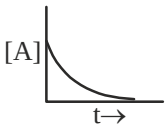
(A) 1 (B) 2 (C) 3 (D) 4/3

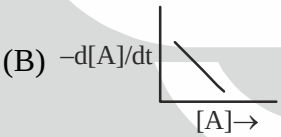
16. The sequence of three steps involved in the following conversion is

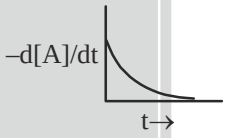


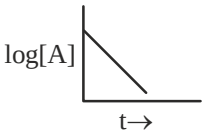
(A) (i) Friedel-Crafts alkylation; (ii) Reduction; (iii) Friedel-Crafts acylation
(B) (i) Friedel-Crafts acylation; (ii) Friedel-Crafts alkylation; (iii) Reduction
(C) (i) Friedel-Crafts acylation; (ii) Reduction; (iii) Friedel-Crafts alkylation
(D) (i) Friedel-Crafts alkylation; (ii) Friedel-Crafts acylation; (iii) Reduction

17. The reaction A $\longrightarrow$ Products, follows first-order kinetics. If [A] represents the concentration of reactant at time t, the INCORRECT variation is the shown in

(A) 

(B) 

(C) 

(D) 

18. The CORRECT order of stability for the following carbocations is

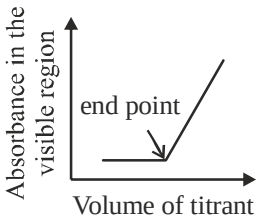
(I) **(II)** **(III)** **(IV)**

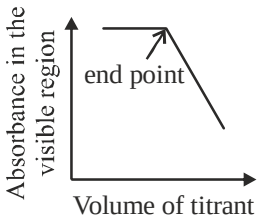
(A) I < III < IV < II (B) III < II < IV < I (C) II < IV < III < I (D) IV < III < I < II

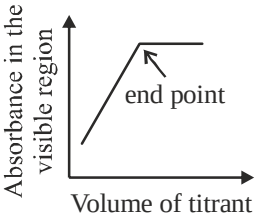
19. The decay modes of ^{14}C and ^{14}O are

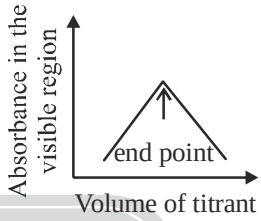
(A) β^- decay
(B) Positron emission
(C) β^- decay and positron emission, respectively
(D) Positron emission and β^- decay, respectively

20. Which plot represents a spectrophotometric titration, where the titrant alone absorbs, light in the visible region?

(A) 

(B) 

(C) 

(D) 

21. The CORRECT order of Δ_0 (the octahedral crystal field splitting of d-orbitals) values for the following anionic metal complexes is

(A) $\left[\mathrm{Ir(CN_6)}\right]^{3-} < \left[\mathrm{Rh(CN)_6}\right]^{3-} < \left[\mathrm{RhI_6}\right]^{3-} < \left[\mathrm{CoI_6}\right]^{3-}$

(B) $\left[\mathrm{CoI_6}\right]^{3-} < \left[\mathrm{RhI_6}\right]^{3-} < \left[\mathrm{Rh(CN)_6}\right]^{3-} < \left[\mathrm{Ir(CN)_6}\right]^{3-}$

(C) $\left[\mathrm{CoI_6}\right]^{3-} < \left[\mathrm{Rh(CN)_6}\right]^{3-} < \left[\mathrm{RhI_6}\right]^{3-} < \left[\mathrm{Ir(CN)_6}\right]^{3-}$

(D) $\left[\mathrm{Ir(CN)_6}\right]^{3-} < \left[\mathrm{CoI_6}\right]^{3-} < \left[\mathrm{Rh(CN)_6}\right]^{3-} < \left[\mathrm{RhI_6}\right]^{3-}$

22. The electrolyte AB_2 ionises in water as

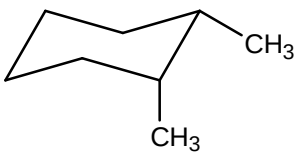
$$AB_2 \rightleftharpoons A^{2+} + 2B^-$$

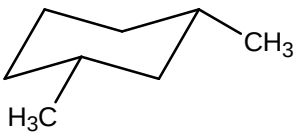
The mean ionic activity coefficient (γ_z)

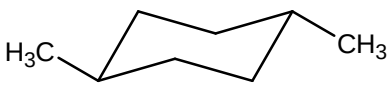
(A) $\gamma_{A^{2+}}^{\frac{1}{2}}\ \gamma_{B^-}$ (B) $\gamma_{A^{2+}}^{\frac{1}{2}}\ \gamma_{B^-}^{\frac{2}{3}}$ (C) $\gamma_{A^{2+}}^{\frac{2}{3}}\ \gamma_{B^-}^{\frac{1}{3}}$ (D) $\left(\gamma_{A^{2+}} + 2\gamma_{B^-}\right)^{1/2}$

23. Among the dimethylcyclohexanes, which one can be obtained in enantiopure form?

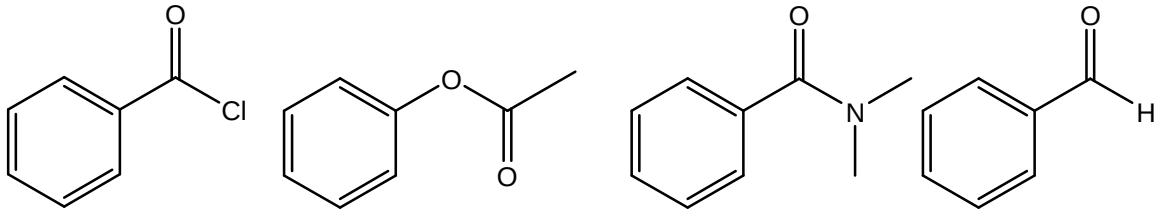
(A) 

(B) 

(C) 

(D) 

24. The CORRECT order of carbonyl stretching frequencies for the following compounds is



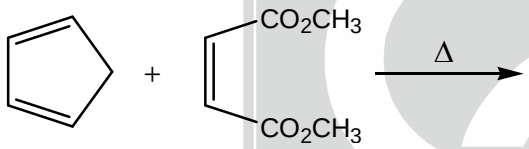
(I) **(II)** **(III)** **(IV)**

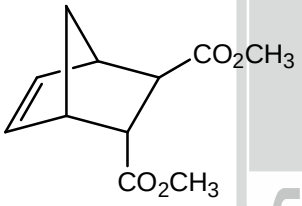
(A) II < I < III < IV (B) I < III < II < IV
(C) IV < II < III < I (D) III < IV < II < I

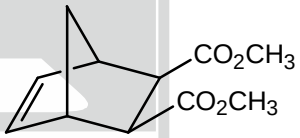
25. The CORRECT expression that corresponds to reversible and adiabatic expansion of an ideal gas is

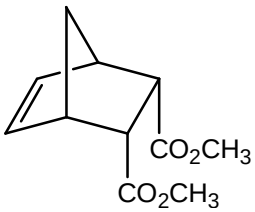
(A) $\Delta U = 0$ (B) $\Delta H = 0$ (C) $\Delta S = 0$ (D) $\Delta G = 0$

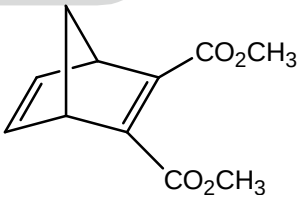
26. The major product formed in the following reaction is



(A)


(B)


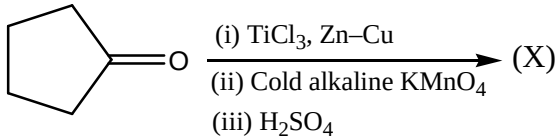
(C)


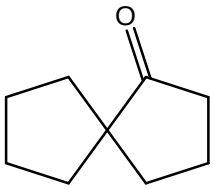
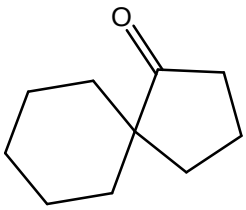
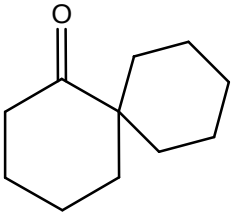
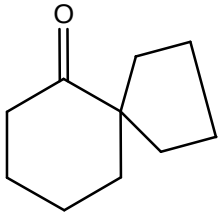
(D)


27. Among the following metal carbonyl species, the one with the highest metal-carbon back bonding is

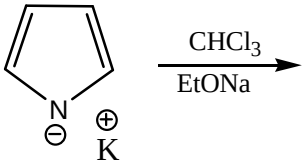
(A) $\left[Ti(CO)_7\right]^{2-}$ (B) $\left[V(CO)_6\right]^{-}$ (C) $Cr(CO)_6$ (D) $\left[Mn(CO)_6\right]^{-}$

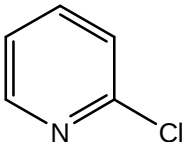
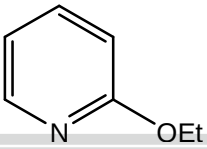
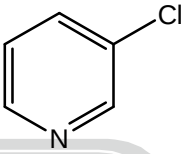
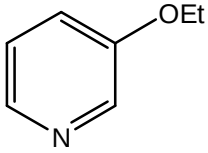
28. The product (X) in the following reaction sequence is



(A)  (B)  (C)  (D) 

29. The major product formed in the following reaction is



(A)  (B)  (C)  (D) 

30. Consider the following four xenon compounds : XeF_2, XeF_4, XeF_4 and XeO_3. The pair of xenon compounds expected to have non-zero dipole moment is

(A) XeF_4 and XeF_6 (B) XeF_2 and XeF_4 (C) XeF_2 and XeO_3 (D) XeF_6 and XeO_3

SECTION-B

Multiple Select Questions (MSQ)

Q.1 – Q.10 carry TWO marks each.

1. The CORRECT statement(s) about carbene is(are)
   (A) Carbene is neutral species
   (B) Carbene is an intermediate in the Curtius rearrangement
   (C) Carbene can insert into both σ and π-bonds
   (D) Carbene is generated from amines on reaction with ntirous acid

2. The CORRECT expression(s) for isothermal expansion of 1 mol of an ideal gas is(are)

   (A) $\Delta A = RT\ell n\dfrac{V_{initial}}{V_{final}}$ (B) $\Delta G = RT\ell n\dfrac{V_{initial}}{V_{final}}$

   (C) $\Delta H = RT\ell n\dfrac{V_{final}}{V_{initial}}$ (D) $\Delta S = RT\ell n\dfrac{V_{final}}{V_{initial}}$

3. Which of the following metal(s) is(are) extracted from its (their) sulfide ore(s) by self-reduction/ air reduction method?
   (A) Cu (B) Al (C) Au (D) Pb

4. Choose the CORRECT answer(s) with respect to the magnesium-EDTA titration carried out in the pH range 7–10.5, using Solochrome black as indicator
   (A) Magnesium-indicator complex is more stable than the magnesium-EDTA complex
   (B) At the end point, the colour changes from red to blue
   (C) After the end point, the colour of the solution is due to the indicator
   (D) pH range of 7-10.5 is necessary for observing the specific colour change

5. Consider the following six solid binary oxides CaO, Al_2O_3, PbO, Cs_2O, SiO_2 and Sb_2O_3. The pair(s) of ionic oxides is(are)
   (A) CaO and Al_2O_3 (B) CaO and PbO
   (C) Cs_2O and Al_2O_3 (D) SiO_2 and Sb_2O_3

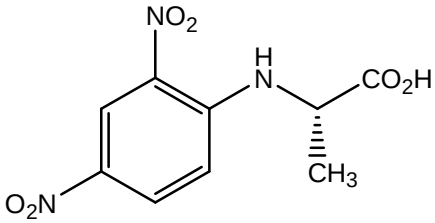
6. In a saturated calomel electrode, the saturation is with respect to
   (A) KCl (B) Hg_2Cl_2 (C) $HgCl_2$ (D) AgCl

7. Which of the following set(s) of quantum numbers is(are) NOT allowed?

(A) $n = 3, \ell = 2, m_\ell = -1$ (B) $n = 4, \ell = 0, m_\ell = -1$

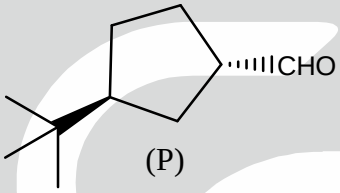
(C) $n = 3, \ell = 3, m_\ell = -3$ (D) $n = 5, \ell = 3, m_\ell = +2$

8. Tetrapeptide(s) that gives (give) the following product on reaction with Sanger's reagent followed by hydrolysis is(are)

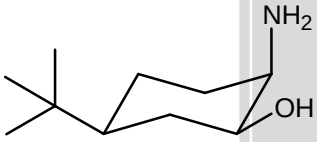


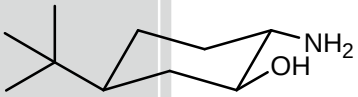
(A) Ala-Gly-Leu-Phe (B) Asp-Phe-Leu-Pro (C) Asp-Gly-Tyr-Phe (D) Ala-Phe-Tyr-Pro

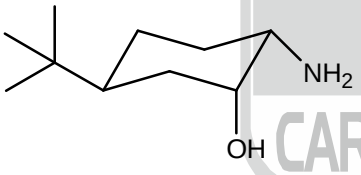
9. One reaction with $NaNO_2$ and HCl, which of the following amino alcohol(s) will yield compound P?

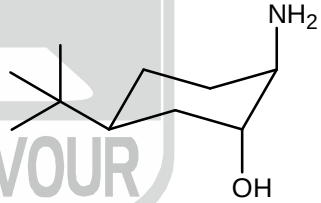


(P)

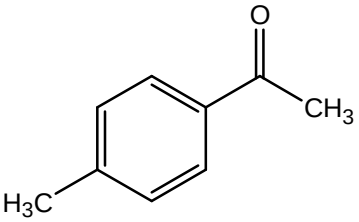
(A) 

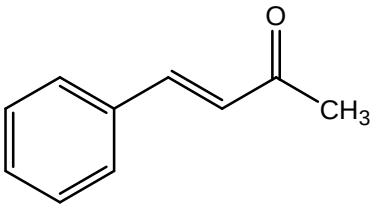
(B) 

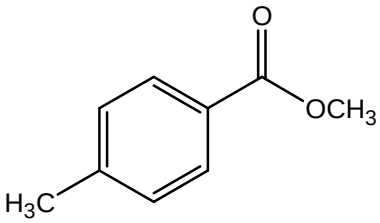
(C) 

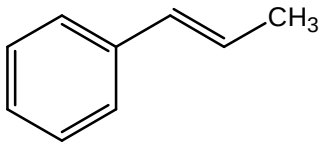
(D) 

10. The compound(s) that shows (show) positive haloform test is(are)

(A) 

(B) 

(C) 

(D) 

SECTION-C

Numerical Answer Type (NAT)

Q.1 – Q.10 carry ONE mark each.

1. Consider the reaction, $CO(g)+\frac{1}{2}O_2(g)\longrightarrow CO_2(g)$

   The value of ΔU for the reaction at 300K is –281.8 kJ mol^{-1}. The value of ΔH at some temperature is _____kJ mol^{-1}(rounded upto the first decimal place)
   (R = 8.3 J K^{-1} mol^{-1})

2. The value of C_v for 1 mole of N_2 gas predicted from the principle of equipartition of energy, ignoring vibrational contribution, is _____ JK^{-1} mol^{-1} (rounded up to two decimal places)

3. The nuclear spin quantum number (I) of a nucleus is 3/2. When placed in an external magnetic field, the number of possible spin energy states it can occupy is _____

4. The time for 50% completion of a zero order reaction is 30 min. Time for 80% completion of this reaction is _____min.

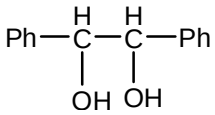
5. The number of possible isomers for [Pt(py)(NH_3)BrCl] is _____(py is pyridine).

6. The volume of 0.3 M ferrous ammonium sulphate solution required for the completion of redox titration with 20 mL of 0.1 M potassium dichromate solution is _____mL

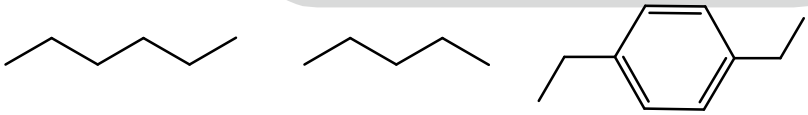
7. The number of hydrogen bond(s) present in a gaunine-cytosine base pair is _____

8. Assuming ideal gas behaviour, the density of O_2 gas at 300K and 1.0 atm is _____gL^{-1} (rounded up to two decimal places)

9. The number of stereoisomers possible for the following compounds is _____



10. Among the following hydrocarbon(s), how many of them would give rise to three groups of proton NMR peaks with 2 : 2 : 3 untegration ratio?



Q.11 – Q.20 carry TWO marks each.

11. For H_2 molecule, the fundamental vibrational frequency $(\bar{\nu}_e)$ in wave numbers can be taken as 4400 cm^{-1}. The zero-point energy of the molecule is _____$kJmol^{-1}$ (rounded up to two decimal places) [h = 6.6×10^{-34} Js, c = 3×10^8 ms^{-1}, N_A = 6×10^{23} mol^{-1}]

12. The electron of a hydrogen atom is in its n^{th} Bohr orbit having de-Broglie wavelength of 13.4Å. The value of n is _____(rounded up to nearest integer)
    [Radius of n^{th} Bohr orbit = 0.53 n^2 Å, $\pi = 3.14$]

13. How many of the following interhalogen species have 2 lone pairs of electrons on the central atom?

    ClF_3, ClF_2^-, ClF_5 and ICl_2^+

14. The magnitude of crystal field stabilization energy (CFSE) of octahedral $[Ti(H_2O)_6]^{3+}$ complex is 7680 cm^{-1}. The wavelength at the maximum absorption (λ_{max}) of this complex is _____nm(rounded up to the nearest integer)

15. For the reaction $H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(\ell)$, the following information is given T = 300K

$\Delta\bar{H}^0 = -285\ kJ\ mol^{-1}$ $\quad \bar{S}^0_{H_2O}(\ell) = 70\ JK^{-1}\ mol^{-1}$

$\bar{S}^0_{O_2}(g) = 204\ JK^{-1}\ mol^{-1}$ $\quad \bar{S}^0_{H_2}(\ell) = 130\ JK^{-1}\ mol^{-1}$

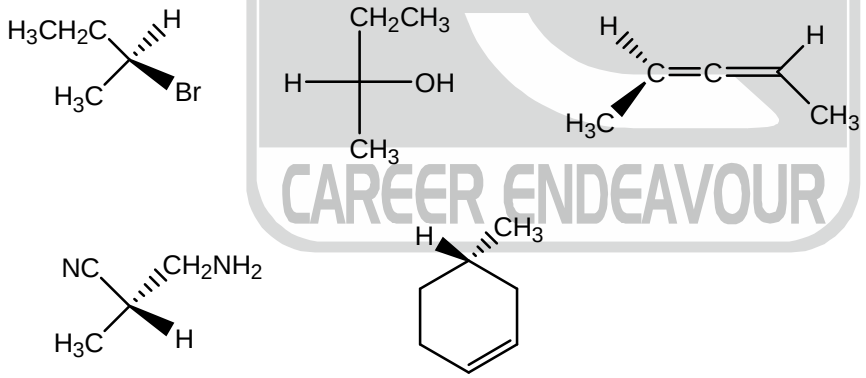
$\Delta\bar{S}^0_{universe}$ for the reaction is _____$JK^{-1}\ mol^{-1}$.

16. ^{24}Na decays to one-fourth of its initial amoount in 29.8 hours. Its decay constant is _____$hour^{-1}$ (rounded up to the four decimal places).

17. Elemental analysis of an organic compound containing C, H and O gives percentage composition C : 39.9% and H : 6.7%. If the molecular weight of the compound is 180, the number of carbon atoms present in the molecule is _____

18. The emf of a standard cadmium cell is 1.02 V at 300K. The temperature coefficient of the cell is $-5.0\times10^{-3}\ VK^{-1}$. The value of ΔH^0 for the cell is _____kJ mol^{-1} (rounded up to two decimal places)
[1F = 96500 C mol^{-1}]

19. The number of compounds having S-configuration among the following is _____



20. The solubility of PbI_2 in 0.10 M KI (aq) is _____$\times10^{-7}$ M (rounded up to two decimal places) (The solubility product $K_{sp} = 7.1\times10^{-9}$]

***** END OF QUESTION PAPER *****