PU-AT/PG-2013
Department of Chemistry, Presidency University, Kolkata 700 073
Booklet Series: D

Subject: Chemistry **F.M.: 100** **Time: 2 Hours**

All questions are of equal value**. For each wrong answer, 0.5 mark will be deducted**. Use of calculator is not permitted

---

1. The standard potentials for the electrode processes Zn^{+2} + 2e = Zn and Cu^{+2} + 2e = Cu are respectively -0.761 and +0.337 V. The reaction : Zn(s) + Cu^{+2} + 2e = Zn^{+2} + Cu is: **(A)** spontaneous**, (B)** non-spontaneous, **(C)** in equilibrium, **(D)** none of these.

2. Jahn-Teller distortion will be noted in (i) $e^4t_2^4$ (ii) $t_{2g}^6e_g^2$ (iii) $t_{2g}^5e_g^2$ (iv) $e^2t_2^2$

(A) I, ii, iii **(B)** ii, iii **(C)** iii, iv **(D)** I, iii, iv

3. The dissociation constants of two acids HA and HB in aqueous solution are 1 x 10^{-3} and 1 x 10^{-5} respectively. How many times HA is stronger than HB? **(A)** 10 times, **(B)** 100 times, **(C)** 1000 times, **(D)** cannot be inferred.

4. A saturated solution of KCl (aq) is used to prepare salt bridge because: **(A)** the speed of K^+ is greater than that of Cl^-, **(B)** the speed of Cl^- is greater than that of K^+, **(C)** the speeds of K^+ and Cl^- are almost equal, **(D)** KCl is highly soluble in water.

5. The plot of log (mean ionic activity coefficient) *vs*. (ionic strength)$^{1/2}$ for a dilute NaCl (aq) solutionl is**: (A)** linear with a positive slope, **(B)** linear with a negative slope, **(C)** independent of ionic strength, **(D)** none of these.

6. The weight-average molecular weight of a system containing equal number of particles of two polymeric samples with molecular weights of M and $2M$ is: **(A)** $3M/5$**, (B)** $5M/3$, **(C)** $3M^2/5$, **(B)** $5M^2/3$.

7. A unit cell of a crystal has the form of a cube. The angle between the normals to the pair of planes whose Miller indices are (010) and (100) is: **(A)** 0^0, **(B)** 45^0, **(C)** 90^0, (**D)** none of the above.

8. The specific conductivity of 0.01 mol dm^{-3} aqueous acetic at 300 K is 19.5 μS cm^{-1} and the limiting molar conductivity of acetic acid at the same temperature is 390 S cm^2 mol^{-1}. The degree of dissociation of this acid is: **(A)** 0.5, **(B)** 0.05, **(C)** 5 x 10^{-3}, **(D)** 5 x 10^{-7}.

9. The vapour pressure of pure liquid A is 0.80 atm. When a nonvolatile substance B as added to A, its vapour pressure drops to 0.60 atm. The mole fraction of B in the solution is: **(A)** 1.00, **(B)** 0.75, **(C)** 0.50, **(D)** 0.25.

10. The half life of a first order reaction is 50 s. Which of the following is correct for this reaction?

(A) The reaction is complete in 100 s, **(B)** the reaction begins after 50 s, **(C)** the quantity of the reactant remaining after 100 s is half of what remained after 50 s**, (D)** none of these.

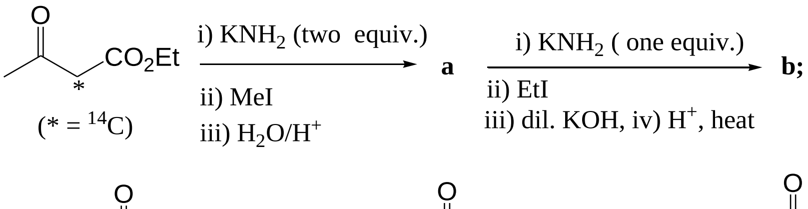
11. The energy (kJ) released when 1.0 g of $_{92}U^{235}+_0 n^1 \rightarrow$ Fission products + Neutrons + 3.20 × 10^7 J is

(A) 12.75 × 10^8 **(B)** 18.60 × 10^8 **(C)** 8.20 × 10^7 **(D)** 6.55 × 10^7

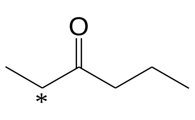
12. Consider the system $2N_2O(g) \Leftrightarrow 2N_2(g) + O_2(g)$, ΔH = +163 kJ. In which direction will an equilibrium system move to reestablish equilibrium if simultaneously N_2O is added, O_2 is removed, the volume is increased and the temperature is raised: **(A)** right**, (B)** left, **(C)** no change, **(D)** difficult to predict.

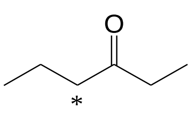
13. The reaction $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$ is spontaneous at 298 K; the reverse reaction becomes spontaneous at high temperature. This means that for the forward reaction: **(A)** both ΔH and ΔS^0 are positive, (B) ΔH is positive, ΔS^0 is negative, **(C)** ΔH is negative, ΔS^0 is positive, **(D)** both ΔH and ΔS^0 are negative.

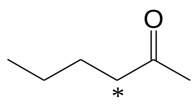
14.

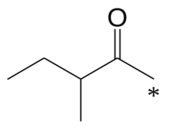


Compound **b** is :

(A)


(B)


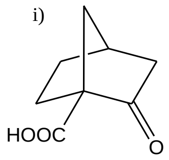
(C)


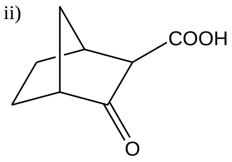
(D)


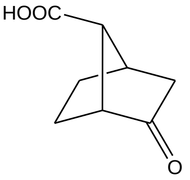
15. The stretching frequency of C-H bond in an organic compound appears at 2900 cm^{-1}. The stretching frequency of C-D bond is: **(A)** 2130 cm^{-1}, **(B)** 3500 cm^{-1}, **(C)** 1450 cm^{-1}, **(D)** 2900 cm^{-1}.

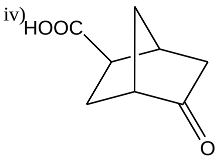
16. Which of the following correctly identifies the mass (*m*) and momentum (*p*) of a photon? **(A)** $m = 0, p = 0$, **(B)** $m = 0, p \neq 0$**, (C)** $m \neq 0, p = 0$, **(D)** $m \neq 0, p \neq 0$.

17. Which of the following compound(s) is/are decarboxylated easily on heating ?

i)


ii)


iii)


iv)


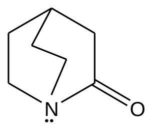
(A) iii only **(B)** I & II **(C)** ii only **(D)** iv only

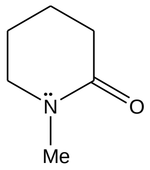
18. The preferred conformation of *trans*- 1,4-dimethylcyclohexane contains the following symmetry elements:
(A) C_2, C_3 **(B)** C2, σ_v **(C)** C_2, σ_{vh} **(D)** C_2, S_4

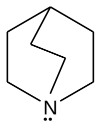
19. A photon of green light collides with a stationary electron. After the collision, the colour of the photon would be**:(A)** unchanged, **(B)** shifted towards red, **(C)** shifted towards blue, **(D)** changed to a colourless state.

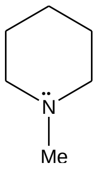
20. A neutron has almost 2000 times the rest mass of an electron. Suppose that they both have 1 eV of energy. How do their wavelengths compare? **(A)** $\lambda(\text{neutron}) = \lambda(\text{electron})$, **(B)** $\lambda(\text{neutron}) > \lambda(\text{electron})$, **(C)** $\lambda(\text{neutron}) < \lambda(\text{electron})$, **(D)** cannot be predicted from the given information.

21. Increasing order of basicity of the following compounds(i-iv) is :

i)


ii)


iii)


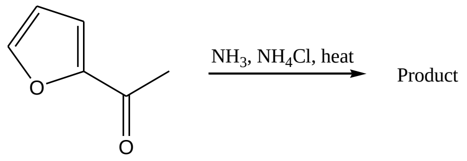
iv)


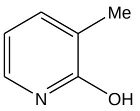
(A) i > iii > iv > ii **(B)** iii > i > iv > ii **(C)** iv > I > iii > ii **(D)** iii > iv > I > ii

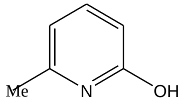
22. For a certain reaction, ΔG^0 is known at two different temperatures. From this information alone, one can calculate for the reaction: **(A)** ΔH, **(B)** ΔS^0, **(C)** both of these, **(D)** none of these.

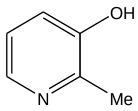
23. The de Broglie wavelength of a particle that has a kinetic energy of E_k is λ. The wavelength is proportional to **(A)** E_k, **(B)** $1/E_k$, **(C)** $1/\sqrt{E_k}$, **(D)** E_k^2.

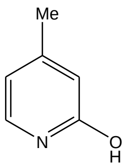
24. Product of the following reaction is:



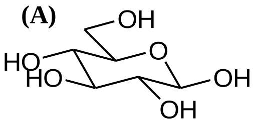
(A)


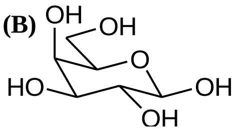
(B)


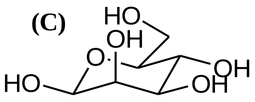
(C)


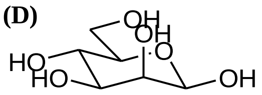
(D)


25. Structure of β-D- Mannose is:

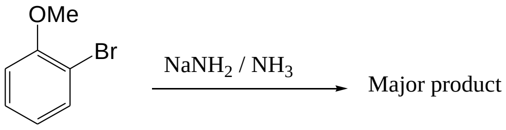
(A)


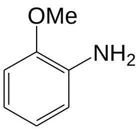
(B)


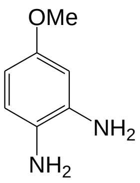
(C)


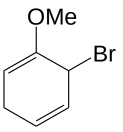
(D)


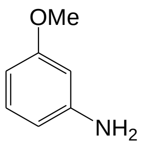
26. Major product formed in the following reaction is



(A)


(B)


(C)


(D)


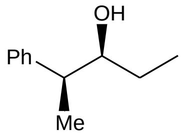
27. Frequency of a line of Lyman spectral series of H atom (R_H = 109600 cm^{-1}) is 82200 cm^{-1}. The transition of the electron is **(A)** 2→1 **(B)** 3→1 **(C)** 4→1 **(D)** 5→1.

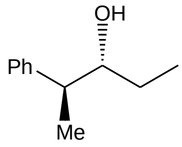
28. A mixture of *p*-N,N-dimethylaminobenzaldehyde (ArCHO) and PhCHO is treated with aqueous ethanolic NaCN. Products formed are**: (A)** ArCH(OH)COAr & PhCH(OH)-COPh **(B)** ArCH(OH)-COAr & PhCH(OH)-COPh & ArCH(OH)-COPh **(C)** ArCO-CH(OH)-Ph & PhCH(OH)-COPh **(D)** ArCO-CH(OH)Ph & PhCO-CO-Ph

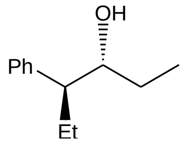
29. The amount of (a,a) form present in the conformational equilibrium of *trans*- 1,2-dichlorocyclohexane (I), *cis*-1,3-dichlorocyclohexane (II) and *trans*- 1,4-dichlorocyclohexane (III) increases as
(A) I < II < III **(B)** II < III < I **(C)** III < I < II **(D)** I < III < II

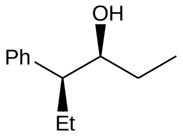
30. The major product of the following reaction is

$$\text{(S)-PhCH(Me)CHO} \xrightarrow{\text{EtMgBr}}$$

(A)


(B)


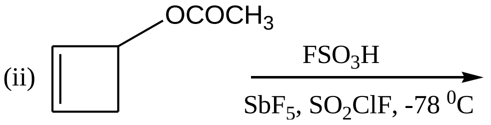
(C)


(D)


31. Binding energy per nucleon (Mev) of $_8O^{16}$ (given: mass of $_8O^{16}$ = 15.9949 amu, $_1H^1$ = 1.007825 amu, and $_0n^1$ = 1.008665 amu) is **(A)** 6.799 **(B)** 8.199 **(C)** 7.977 **(D)** 7.177

32. The species **X** and **Y** in the following schemes are respectively

(i) [8] Annulene $\xrightarrow{SbF_5,\ SO_2ClF,\ -78\ ^0C}$ **X**



(A) aromatic, antiaromatic **(B)** nonaromatic, aromatic **(C)** aromatic, homoaromatic **(D)** antiaromatic, homoaromatic

33. Which of the following statements is correct? **(A)** LUMO energy of ethene is greater than that of 1,3-butadiene. **(B)** HOMO energy of ethene is greater than that of 1,3-butadiene. **(C)** HOMO of allyl cation is a nonbonding orbital **(D)** HOMO of allyl anion is an antibonding orbital.

34. Treatment of an acidic silicate solution with excess ammonium molybdate gives a yellow coloration. The composition of the yellow compound is

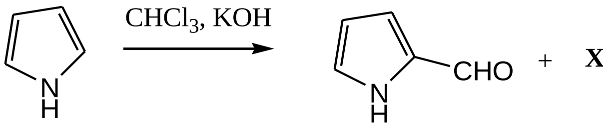
(A) $Si(OH)_4. (MoO_3)_{12}$ **(B)** $H_2SiO_3. (MoO_3)_{12}$ **(C)** $(NH_4)_2SiO_3. Mo_{12}O_{40}$ **(D)** no specific composition.

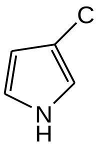
35. Treatment of a black precipitate (X) with aquaregia gives colourles solution (Y) which when treated with insufficient stannous chloride gives white precipitate (Z). Identify X, Y and Z.

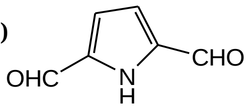
(A) Hgs, $HgCl_4^{2-}$, Hg_2Cl_2 **(B)** Ag_2S, $AgCl_2^-$, AgCl **(C)** CoS, $CoCl_4^-$, $CoCl_2$ **(D)** CuS, $CuCl_4^{2-}$, CuCl

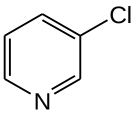
36. When anisole is cleaved with HI the product formed will be: **(A)** Iodobenzene and methanol **(B)** Phenol and methyl iodide **(C)** Iodobenzene, phenol and methyl iodide **(D)** None of this

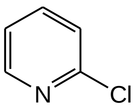
37. The species **X** in the following schemes is



(A) 

(B) 

(C) 

(D) 

38 (i) –CH(OMe)OH (ii) –CHO (iii) $–CH_2CMe_3$ (iv) $–CH_2CH(Me)CH_2OH$

Increasing order of of the above groups according to CIP rule is:

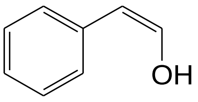
(A) ii > i > iv > iii **(B)** i >.ii > iii > iv **(C)** ii > iv > i > iii **(D)** i > iv > ii > iii

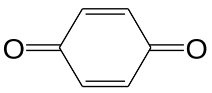
39. Values of formal charge on N, C and S atoms in H-N=C=S is: **(A)** 1-, 0,0 **(B)** 1+, 0, 0 **(C)** 0, 0, 1+ **(D)** 0, 1+,0.

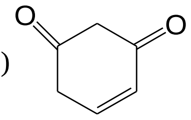
40. The p orbitals of M in ML_2 complex (bond axis = z –axis) will have energy order

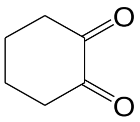
(A) $p_x = p_y = p_z$ **(B)** $p_x>p_y>p_z$ **(C)** $p_x = p_z<p_y$ **(D)** $p_x = p_y<p_z$

41. Among **a, b, c, d**, tautomerism is exhibited by:

(a) 

(b) 

(c) 

(d) 

(A) a only **(B)** a, b, c **(C)** a, c. d **(D)** b, c, d

42. Arrangement of the following with increasing effective magnetic moment (BM) value of (i) NiF_6^{2-} (ii) CoF_6^{3-} (iii) CuF_6^{3-} (iv) $MnF_6^{4-}$is (A) iv > ii >iii > I (B) i< ii < iii < iv (C) iv < ii < iii <i (D) iii > ii >i> iv .]

43. Which one will be the Russel Saunders term (lowest energy) in d^5 high spin complex?

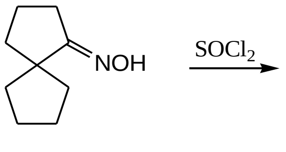
(A) $^6T_{2g}$ **(B)** ^6E_g **(C)** $^6T_{1g}$ **(D)** $^6A_{1g}$

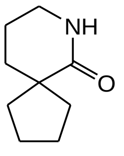
44. The orbitals of As used for hybridization in AsF_5 are

(A) d_{z2}, s, p_x, p_y, p_z **(B)** d_{x2-y2}, s, p_x, p_y, p_z **(C)** s, p_x, p_y, p_z,d_x **(D)** s, p_x, p_y, p_z, d_{z2}

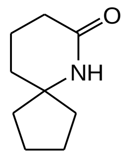
45. Bond order of O_2^+, O_2^-, O_2^{2-} are : **(A)** 1.0, 2.5, 1.5 **(B)** 1.5, 2.5, 1.0 **(C)**2.5, 1.5, 1.0 **(D)** 2.5, 1.0, 1.5.

46. The following rearrangement reaction yields

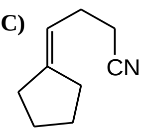


(A) 

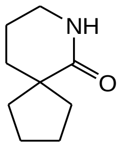
only

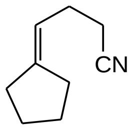
(B) 

only

(C) 

only

(D) 

and 

47. Assuming hydrogen ion concentration unity throughout the experiment, the equivalent potential (in Volt) for the titration of 100.0 ml 0.1 (N) Fe^{2+} with 0.1 (N) $KMnO_4$ will be [Given: E^0 for Fe^{3+}/Fe^{2+} = 0.77 V and for MnO_4^-/Mn^{2+} = 1.51V]: **(A)** 1.51 **(B)** 0.77 **(C)** 1.39 **(D)** 0.343

48.The CFSE values in Dq_0 (Neglect P) of $[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$, and $[Cu(NH_3)_6]^{2+}$ will be

(A) 4, 24, 6 **(B)** 24, 24, 6 **(C)** 4, 4, 6 **(D)** 24, 4, 6

49. Which statement is incorrect about CO ligands?

(A) A CO ligand can accept electrons into its π* MO; this weakens the C–O bond **(B)** In the IR spectrum of $Fe(CO)_5$, absorptions assigned to the CO stretching modes are at higher wave number than that of free CO **(C)** CO ligands can adopt terminal, μ and μ_3 bonding modes; the amount of back donation depends on the bonding mode **(D)** Fluxional behavior is common in metal carbonyl compounds, and can be investigated by ^{13}C NMR spectroscopy

50. N-O bond length in NO^+, NO and NO^- species is in the order

(A) $NO^+< NO < NO^-$ **(B)** $NO^+> NO >NO^-$ **(C)** $NO^+> NO^->NO$ **(D)** $NO^+< NO^-< NO$

----------------X----------------