A

2005 – CH

Test Paper Code : CH

Time : 3 Hours **Max. Marks : 300**

INSTRUCTIONS

1. The question-cum-answer book has **32** pages and has **44** questions. Please ensure that the copy of the question-cum-answer book you have received contains all the questions.
2. Write your **Roll Number, Name and the name of the Test Centre** in the appropriate space provided on the right side.
3. Write the answers to the objective questions against each Question No. in the **Answer Table for Objective Questions**, provided on page No. **11**. Do not write anything else on this page.
4. Each objective question has **4 choices** for its answer: (A), (B), (C) and (D). Only **ONE** of them is the correct answer. There will be **negative marking** for wrong answers to objective questions. The following marking scheme for objective questions shall be used :
   (a) For each objective question, you will be awarded **3 (three)** marks if you have written only the correct answer.
   (b) In case you have not written any answer for a question you will be awarded **0 (zero)** mark for that question.
   (c) In all other cases, you will be awarded **–1 (minus one)** mark for the question.
5. Answer the subjective question only in the space provided after each question.
6. Do not write more than one answer for the same question. In case you attempt a subjective question more than once, please cancel the answer(s) you consider wrong. Otherwise, the answer appearing later only will be evaluated.
7. All answers must be written in blue/black/blue-black ink only. Sketch pen, pencil or ink of any other colour should not be used.
8. All rough work should be done in the space provided and scored out finally.
9. No supplementary sheets will be provided to the candidates.
10. **Logarithmic Tables / Calculator of any kind / cellular phone / pager / electronic gadgets are not allowed.**
11. The question-cum-answer book must be returned in its entirety to the Invigilator before leaving the examination hall. Do not remove any page from this book.

Invigilator

Invigilator

A

2005 – CH

READ THE INSTRUCTIONS ON THE LEFT SIDE OF THIS PAGE CAREFULLY

ROLL NUMBER					

Name :

Test Centre :

Do not write your Roll Number or Name anywhere else in this question-cum-answer book.

I have read all the instructions and shall abide by them.

.....

Signature of the Candidate

I have verified the information filled by the Candidate above.

.....

Signature of the Invigilator

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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.

Write the answers to the objective questions ONLY in the *Answer Table for Objective Questions* provided on page 11.

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

(i) $CH_3COC\boldsymbol{H}_3$

(ii) $CH_3COC\boldsymbol{H}_2COCH_3$

(iii) $CH_3OOCC\boldsymbol{H}_2COOCH_3$

(iv) $CH_3COC\boldsymbol{H}_2NO_2$

(A) (ii) > (iii) > (i) > (iv)

(B) (iv) > (ii) > (iii) > (i)

(C) (iv) > (iii) > (ii) > (i)

(D) (ii) > (iv) > (iii) > (i)

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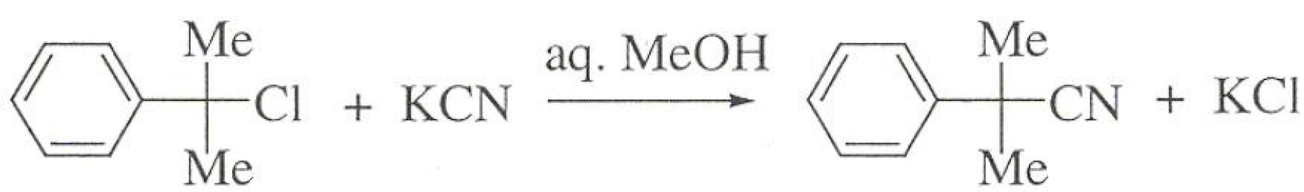
2. For the reaction shown below if the concentration of KCN is increased four times, the rate of the reaction will be



(A) doubled

(B) increased four times

(C) unaffected

(D) halved

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

Nucleophiles : $HO^{\ominus}$, $CH_3COO^{\ominus}$, $PhO^{\ominus}$, $CH_3O^{\ominus}$

(A) $CH_3O^{\ominus} > HO^{\ominus} > PhO^{\ominus} > CH_3COO^{\ominus}$

(B) $HO^{\ominus} > CH_3O^{\ominus} > PhO^{\ominus} > CH_3COO^{\ominus}$

(C) $HO^{\ominus} > PhO^{\ominus} > CH_3O^{\ominus} > CH_3COO^{\ominus}$

(D) $CH_3COO^{\ominus} > CH_3O^{\ominus} > HO^{\ominus} > PhO^{\ominus}$

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) $BrCH_2CH{=}CHCH_2Br$

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6. The reaction of (+) 2-iodobutane and NaI^* (I^* is radioactive isotope of iodine) in acetone 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) $k_i = (1/3) \times k_r$

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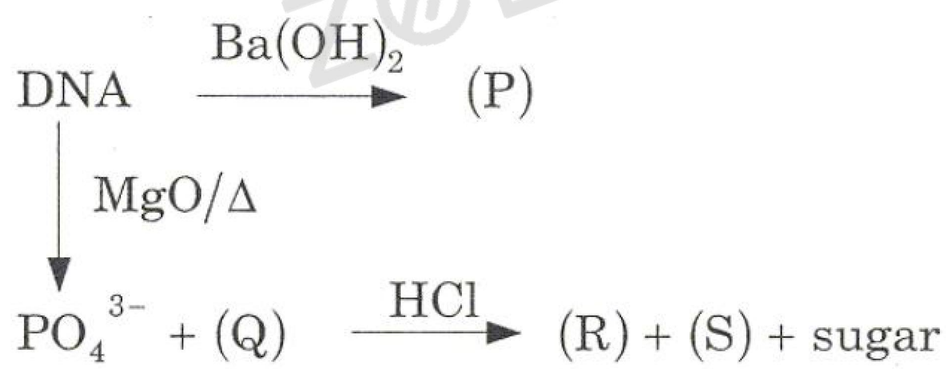
7.



In the scheme shown above (P), (Q), (R) and (S) are

(A) (P) = purine bases, (Q) pyrimidine bases, (R) = nucleotides, (S) = nucleosides

(B) (P) = (Q) = nucleotides, (R) = pyrimidine bases, (S) = purine bases

(C) (P) = nucleosides, (Q) = nucleotides, (R) = (S) = purine bases

(D) (P) = nucleotides, (Q) = nucleosides, (R) = pyrimidine bases, (S) = purine bases

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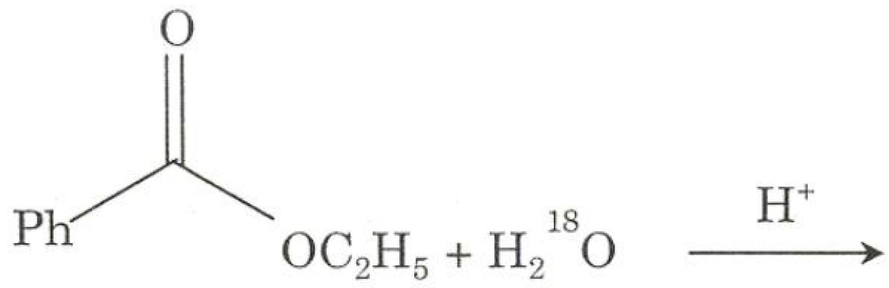
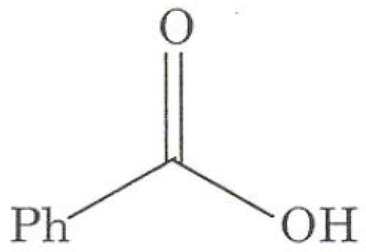
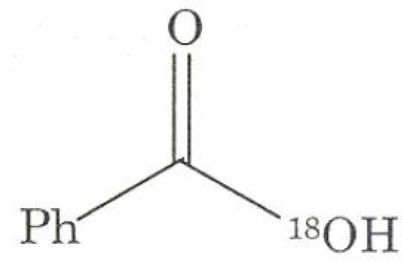
8. The products obtained from the following reaction are

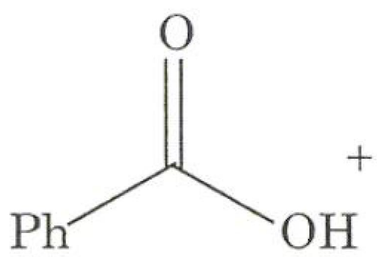


(A) 

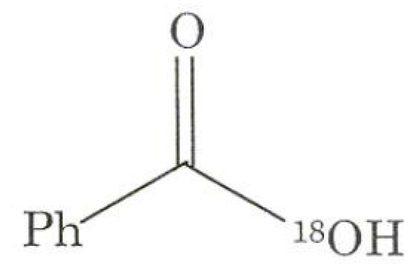
$+ C_2H_5OH$

(B) 

$+ C_2H_5OH$

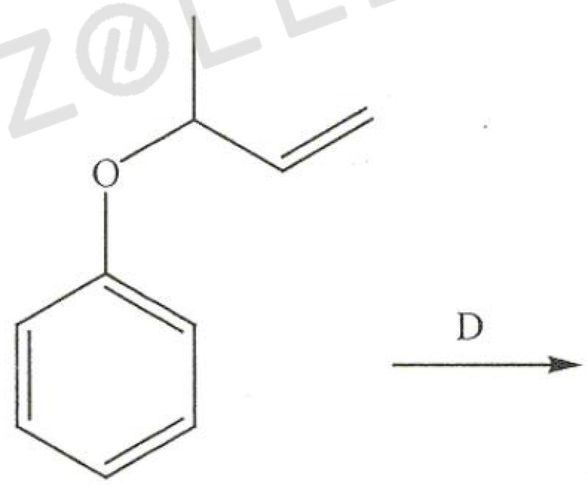
(C) 

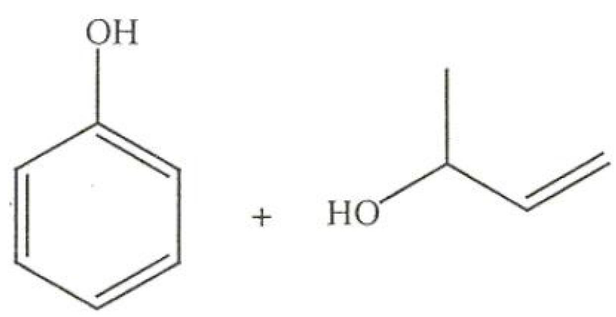
$+ C_2H_5{}^{18}OH$

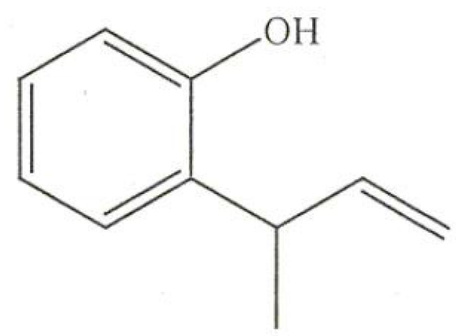
(D) 

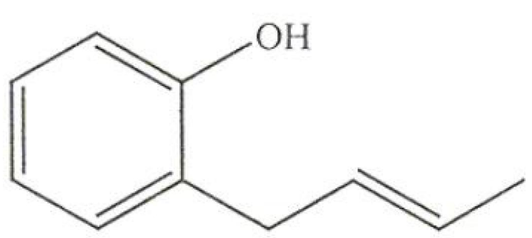
$+ C_2H_5{}^{18}OH$

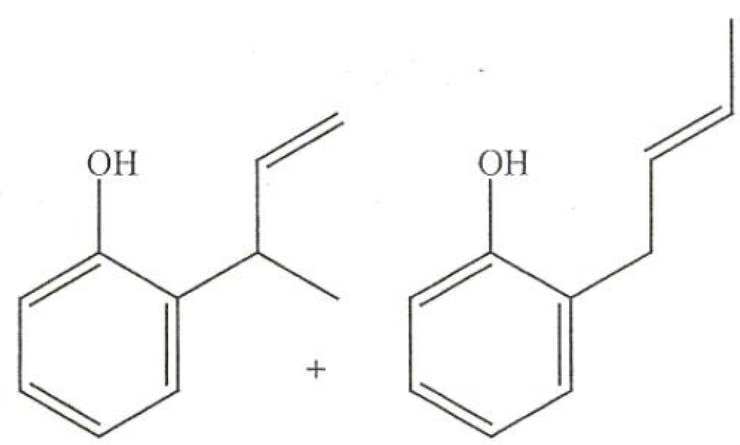
9. The product(s) obtained in the following reaction is (are)



(A) 

(B) 

(C) 

(D) 

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10. Match the isoelectric points 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) – (II), (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 planar

(D) octahedral

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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) ${}^{13}_{6}C$

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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) $\frac{-9}{5}\Delta_0 + 3P$

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17. The complex with the most intense 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) $Ag_2S_2O_3$

(D) Ag_2SO_4

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19. Among the following complexes,

(i) $[Ru(bipyridyl)_3]^+$

(ii) $[Cr(EDTA)]^-$

(iii) *trans*$-[CrCl_2(oxalate)_2]^{3-}$

(iv) *cis*$-[CrCl_2(oxalate)_2]^{3-}$

the ones that show chirality are

(A) (i), (ii), (iv)

(B) (i), (ii), (iii)

(C) (ii), (iii), (iv)

(D) (i), (iii), (iv)

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20. The electronic configurations that have orbital angular momentum contribution in an 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 :

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

and the equilibrium constant K_2 for the reaction :

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \text{ is}$$

(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.

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24. The value of the 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. The order of the reaction is

(A) 0

(B) 1

(C) 2

(D) 3

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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 uncertainty is 1×10^{-10} m, the uncertainty in the 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}

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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 the following (where v_{mp}, v_{av} and v_{rms} are the most probable velocity, average velocity and 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) $v_{mp} > v_{av} > v_{rms}$

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

(A) 1.21 V

(B) 0.33 V

(C) −0.036 V

(D) 0.036 V

Space for rough work

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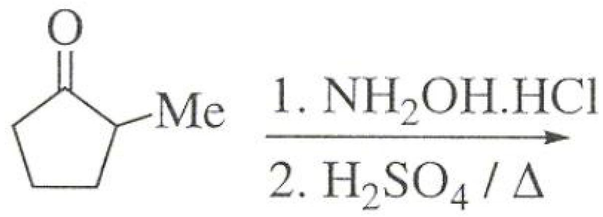
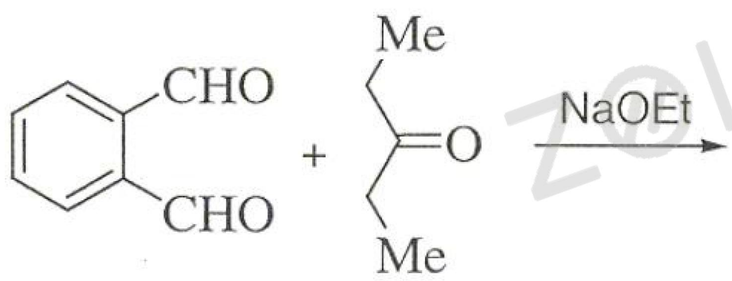
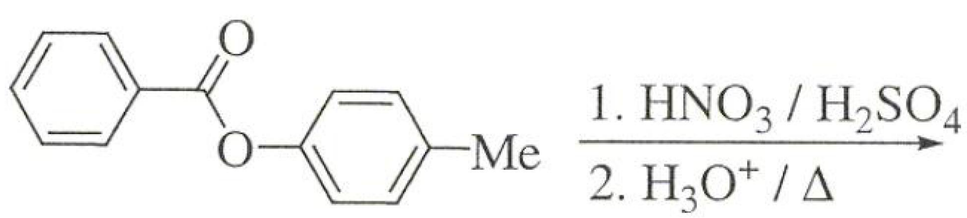
31. Identify the major product(s) formed in the following reactions. ***Intermediates and reaction mechanisms need not be discussed.***

(a) 

(6)

(b) 

(6)

(c) 

(3)

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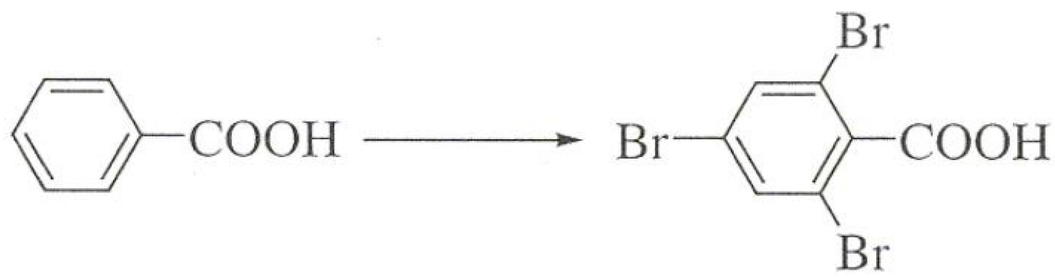
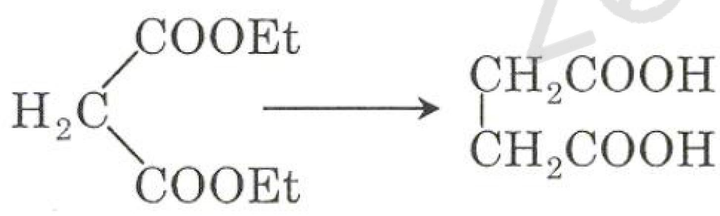
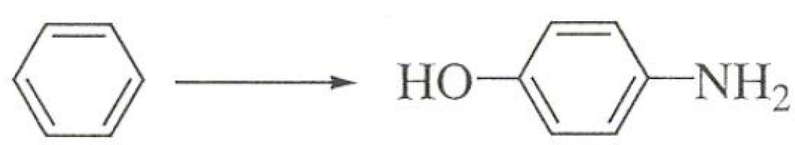
32. How may the following transformations be effected? Indicate the reagents / reaction conditions clearly in each step.

(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)

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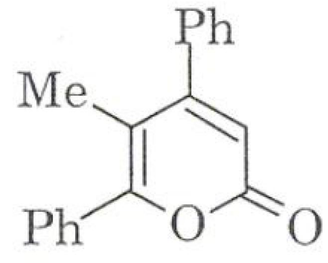
33. Suggest a suitable mechanism for each of the following reactions.

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

(6)

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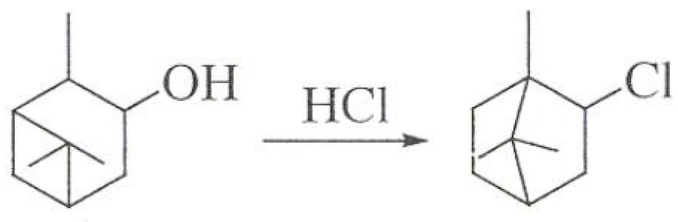
(b) 

(9)

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34. Rationalize the following observations using suitable mechanisms.

(a) Nitration of 4-*t*-butyltoluene gives 4-nitrotoluene as one of the products. (3)

(b) *cis*-4-*t*-Butylcyclohexyltrimethylammonium hydroxide undergoes Hoffman elimination to yield 4-*t*-butylcyclohexene whereas the *trans* isomer does not (use conformations to explain). (6)

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

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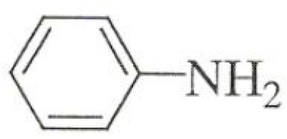
35. (a) Suggest a chemical method for the separation of a mixture containing *p*-N,N-dimethylaminophenol and *p*-aminobenzoic acid and give a confirmatory test for phenol. (6)

(b) Write the structures of X, Y and Z in the following. (9)

(i) 

$\xrightarrow[\text{2. β-naphthol / NaOH}]{\text{1. NaNO}_2\text{ / dil. HCl, 0 °C}}$ X

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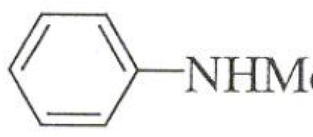
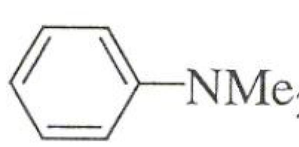
(ii) 

$\xrightarrow{\text{NaNO}_2\text{ / dil. HCl}}$ Y

(iii) 

$\xrightarrow{\text{NaNO}_2\text{ / dil. HCl}}$ Z

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36. (a) Predict the hybridization and draw the structure of the following molecules based on VSEPR theory : (i) I_3^- (ii) SO_3^{2-} (iii) $P(CH_3)_3F_2$ (9)

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

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

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

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(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 $Zn(NO_3)_2$

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

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

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

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39. (a) The radioactive element Ra (Z = 88) emits three alpha particles in succession. Deduce in which group the resulting element will be found? (6)

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(b) A radioisotope sample has an initial activity of 23 dis/min. After $\frac{1}{2}$ h, the activity is 11.5 dis/min. How many atoms of the radioactive nuclide were present originally? $[\alpha t_{1/2} = 0.69]$ (9)

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

(i) $CH_3I + HO^- \longrightarrow$

(ii) $CF_3I + HO^- \longrightarrow$

(iii) $2CF_3I + Na[Mn(CO)_5] \longrightarrow$

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

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41. Justify the following : (15)

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

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(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.

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

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

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42. The rate constant k for a second order reaction $P + Q \rightarrow$ Products is expressed as $\log_{10} k = 20 - \frac{3000}{T}$, 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)

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43. The equilibrium constant for the reaction

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

at 600°C is 1.00. If a mixture initially consisting of 1 mole of Fe_3O_4, 2 moles of CO, 0.5 mole of FeO and 0.3 mole of CO_2 is heated to 600°C at constant total pressure of 5 atmospheres, how many moles of each substance would be present at equilibrium? (15)

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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)

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(b) At 20°C, the vapor 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 fractions of X and Y in the vapor phase in equilibrium with the solution. (6)

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