JAM 2006

CHEMISTRY TEST PAPER

Useful Data

$2.303\frac{RT}{F} = 0.059\ \text{V at } 298.15\ \text{K}$

$R = 8.3145\ \text{J.mol}^{-1}\ \text{K}^{-1}$

$F = 96500\ \text{C.mol}^{-1}$

$K_W = 10^{-14}$ at 298.15 K

$m_e = 9\times10^{-31}\ \text{kg}$

$K_f = 1.8\ ^\circ\text{C}/m$ for water

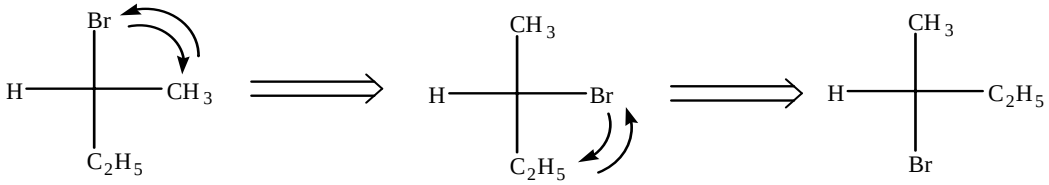
$h = 6.6\times10^{-34}\ \text{J.s}$

$\ln 2 = 0.69$

Atomic number of Ti = 22, Cr = 24, Co = 27

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 in the *Answer Table for Objective Questions* provided on page 13 only.

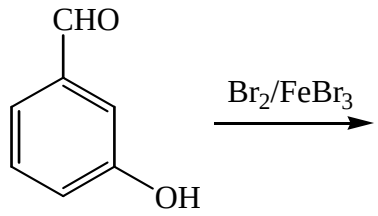
1. After the following interchanges of groups in the Fischer projection of 2-bromobutane, the configuration of (X) and (Y) will be



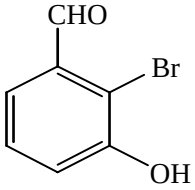
(X) (Y)

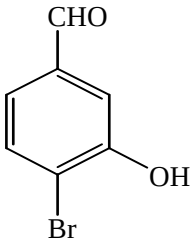
(A) X = R; Y = S (C) X = R; Y = R
(B) X = S; Y = R (D) X = S; Y = S

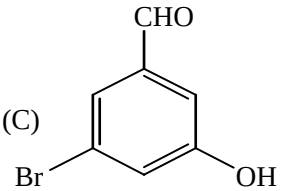
2. The major product of the reaction

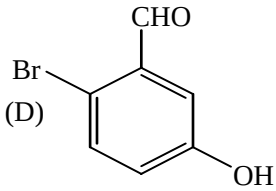


is

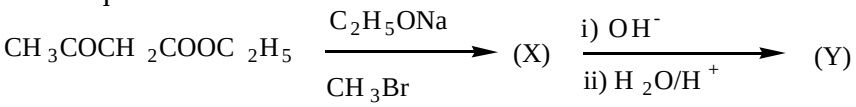
(A) 

(B) 

(C) 

(D) 

3. In the reaction sequence



the product (Y) is

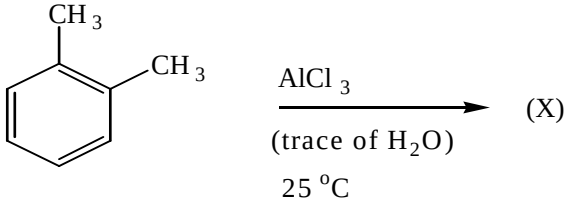
(A) $CH_3COCH_2COOCH_3$

(C) $CH_3COCH(CH_3)_2$

(B) $CH_3COCHCOOH$ (with CH_3 branch)

(D) $CH_3COC_2H_5$

4. The major product (X) in the reaction



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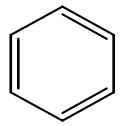
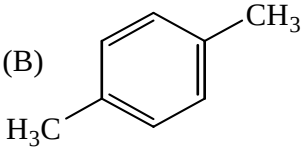
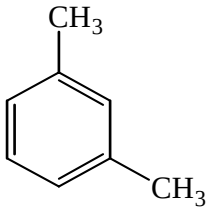
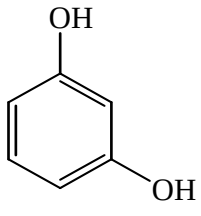
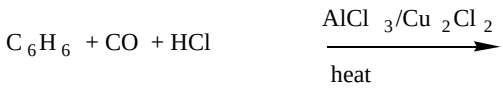
(A) 

(B) 

(C) 

(D) 

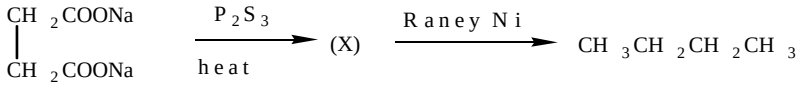
5. The product of the reaction



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



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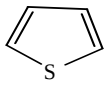
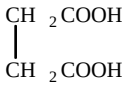
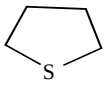
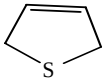
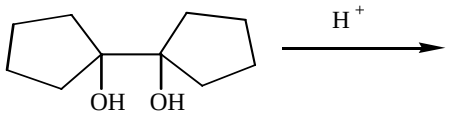
(A) 

(B) 

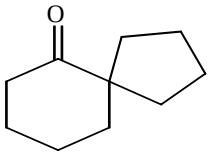
(C) 

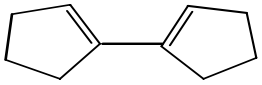
(D) 

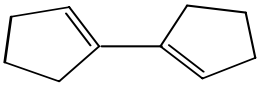
7. The major product of the reaction

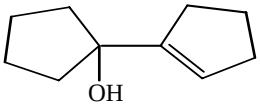


is

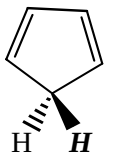
(A) 

(C) 

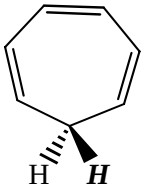
(B) 

(D) 

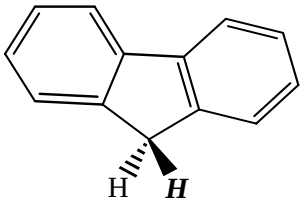
8. The increasing order of the acidity of the hydrogen marked in ***bold italics*** among the following is



I



II



III

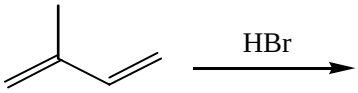
(A) III < II < I

(C) II < I < III

(B) I < II < III

(D) II < III < I

9. The major product of the reaction



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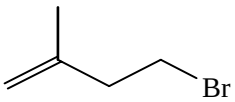
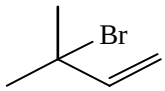
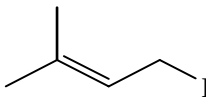
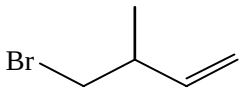
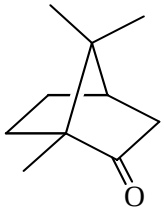
(A) 

(C) 

(B) 

(D) 

10. The number of enantiomers of camphor



is

(A) Four

(C) Two

(B) Three

(D) One

11. The decreasing order of the first ionization energy of the following elements is

(A) He > H > Be > B

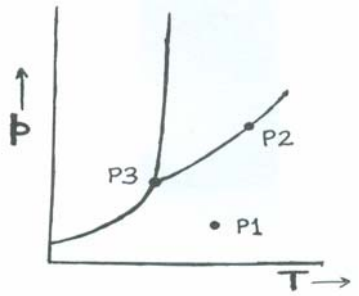
(B) Be > B > H > He

(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 the ionic nature of the following compounds 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 phosphorus 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_o) of *d* orbital energies of the following 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 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

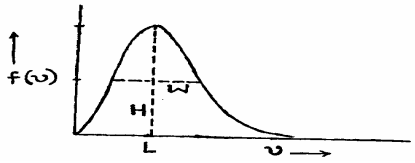
25. The statement that is correct for both electrochemical (galvanic) cells and electrolytic cells is
(A) $\Delta G = - nFE$
(B) Free energy decreases in both cells
(C) The cell potentials are temperature independent
(D) Chemical energy is converted into electrical energy in both cells

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 wavefunction 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 $[Cu(CH_3CN)_4]^+$ 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.

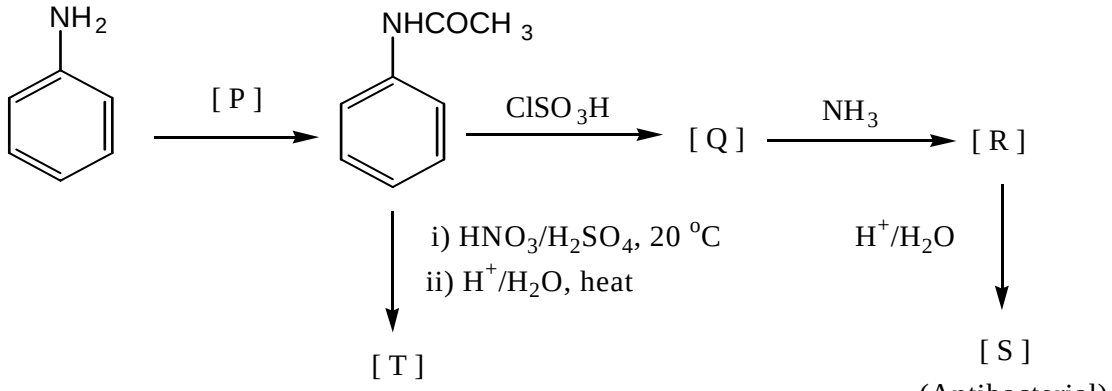


In the figure, H is the height of the peak, L is the location of the maximum and W is the width at half height. As the temperature is decreased,

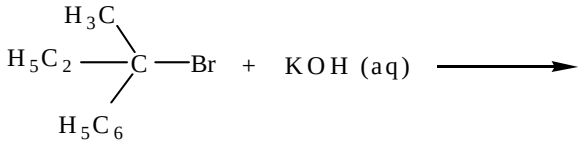
(A) H increases, L decreases and W increases
(B) H increases, L decreases and W decreases
(C) H decreases, L decreases and W increases
(D) H decreases, L decreases and W decreases

30. A system undergoes two cyclic processes 1 and 2. Process 1 is reversible and process 2 is irreversible. The correct statement relating to the two processes is
(A) ΔS (for process 1) = 0, while ΔS (for process 2) $\neq 0$
(B) $q_{cyclic} = 0$ for process 1 and $q_{cyclic} \neq 0$ 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 reactions (15)



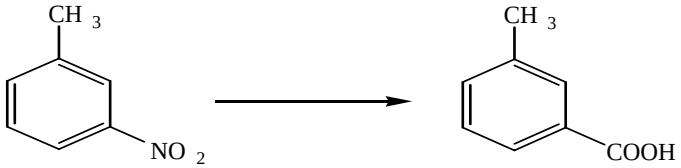
32. For the reaction



(dextro)

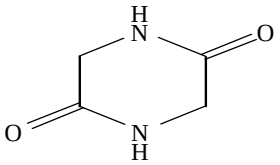
i) what is the optical activity of the product?
ii) draw the energy profile for the reaction
iii) write the structure of the intermediate
iv) what is the effect of doubling the concentration of KOH on the rate of the reaction?
v) if aqueous KOH is replaced by alcoholic KOH, write the structure of the product formed. (15)

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

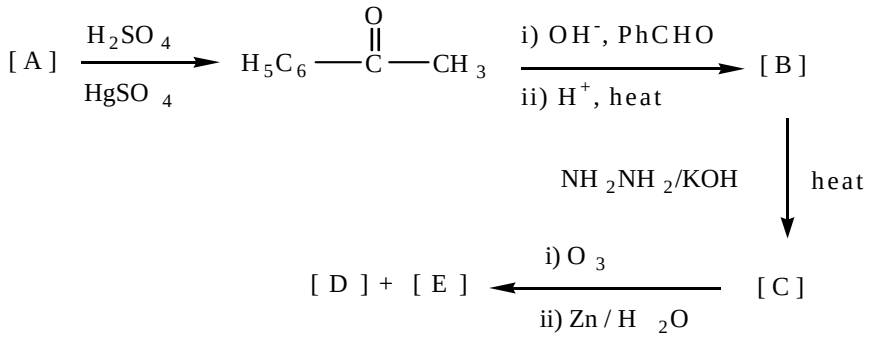


Indicate the reagents/reaction conditions required at each step clearly. (6)

(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. (9)



34. Identify the compounds A, B, C, D and E in the following reactions (15)



35. (a) Why do the boiling points of the following compounds vary in the order, $H_2O > H_2Se > H_2S$? (6)

(b) Identify the products in the reaction of CCl_4 and $SiCl_4$ with water. Justify your answer. (9)

36. (a) Write the steps involved in the production of pure elemental silicon from silica. (9)

(b) Both the products A and B, in the following reactions, contain boron and nitrogen. Identify A and B. (6)

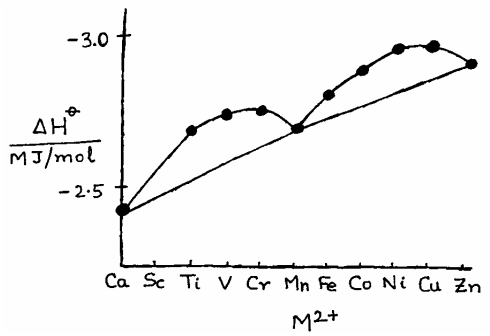
$$3\,NH_4Cl + 3\,BCl_3 \xrightarrow[\text{heat}]{C_6H_5Cl} A \xrightarrow[\text{THF}]{LiAlH_4} B$$

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 trisoxalatochromate(III). (i) Write the chemical formula of the chromium complex formed. (ii) Write the balanced chemical equation for the formation of the complex. (iii) Calculate the room temperature spin-only magnetic moment, in Bohr magnetons, of the complex. (9)

(b) Write the structures of possible isomers of $[CoCl_2(en)_2]Cl$ (6)

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. (9)

(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? (6)



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 deuterated alanine, $H_2N\text{-}CH(CD_3)\text{-}COOH$, was added. After thorough mixing, some of the alanine was separated 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? (6)

(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. (9)

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. (9)

(b) One mole of a salt of type MX is dissolved in 1.00 kg of water. The freezing point of the solution is –2.4 °C. Calculate the percent dissociation of the salt in water. (6)

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

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

Determine the Arrhenius activation energy for the reaction, assuming that the frequency factor does not change in this temperature range. (6)

(b) Ozone seems to be formed in the atmosphere through the photolysis of diatomic molecule:

$$O_2 \xrightarrow[h\nu]{k_o} 2\,O$$

$$O + O_2 \xrightarrow{k_1} O_3$$

$$O_3 + O \xrightarrow{k_2} 2\,O_2$$

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. (9)

42. (a) The reaction $N_2 + 3\,H_2 \rightarrow 2\,NH_3$ 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? (6)

(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 S cm^2 mol^{-1}, respectively. 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. (9)

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

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

Determine the most probable radial distance for the electron in this state and also the position of the node (in terms of a_o). (9)

(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 $E_n = n^2h^2/8ma^2$). (6)

44. (a) Solve the differential equation $y'' - 5y' + 6y = 0$ with the initial 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. (9)

(b) For a particle with position $\mathbf{r} = 2\mathbf{i} - 3\mathbf{j} + \mathbf{k}$ and momentum $\mathbf{p} = \mathbf{i} + 2\mathbf{j} - 2\mathbf{k}$ in m and kg.m.s^{-1}, respectively, calculate the magnitude of the angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. (6)