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2021

CHEMISTRY

PAPER-I

Time Allowed — 3 Hours *Full Marks — 200*

If the questions attempted are in excess of the prescribed number, only the questions attempted first up to the prescribed number shall be valued and the remaining ones ignored.

The figures in the margin indicate full marks for each question.

Answers may be written either in ***English*** *or in* ***Bengali*** *but all answers must be in one and the same language.*

Section-I

This Section comprises 15 questions in three Groups.
Answer *any ten* questions taking *at least three* questions from each Group.

Group-A

1. Following Bohr model what will be the size of Ne^{9+} ion? Is the size greater than the H-atom? 3+1=4
2. Between Cu(I) chloride and Au(I) chloride which one has higher melting point? Justify your answer. 2+2=4
3. Using VSEPR theory predict the structure of XeF_2 with proper explanation, mentioning the hybrid orbital used by the central atom. 3+1=4
4. An aqueous solution of ammonium acetate reacts neutral to litmus. Why? 4
5. Tl in its 2+ oxidation state is typically unstable. Explain. 4

Group-B

6. Increase of pressure and lowering in temperature may lead to transformation of a gas into liquid. Among these two factors which one do you consider more important and why? 4
7. With an increase in temperature viscosity of a liquid decreases while that of a gas increases — Justify or criticise. 4
8. With an example write down the steps to convert Weiss indices to Miller indices of a crystal system. 4

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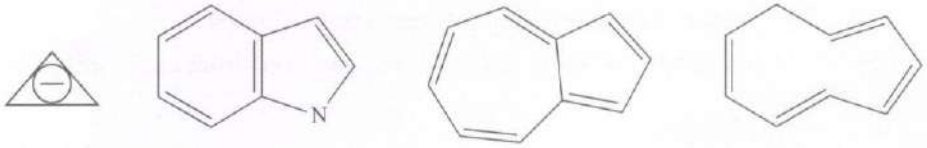
9. Draw a model Maxwell's speed distribution curve of a gaseous system and indicate on it the positions of C_m, C_a and C_{rms} where the terms refer to most probable, average and root mean square speeds of the gas. 4

10. Calculate the minimum work needed to prepare 1kg ice from water at 25°C in a refrigerator working between –5°C and 25°C. (Latent heat of fusion of ice = 80 cal g^{-1}.) 4

Group-C

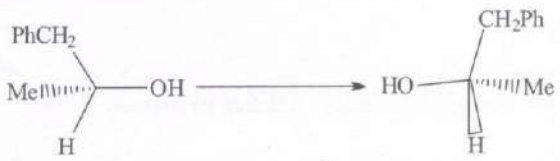
11. Classify the following as aromatic, antiaromatic and nonaromatic. 4



(i) (ii) (iii) (iv)

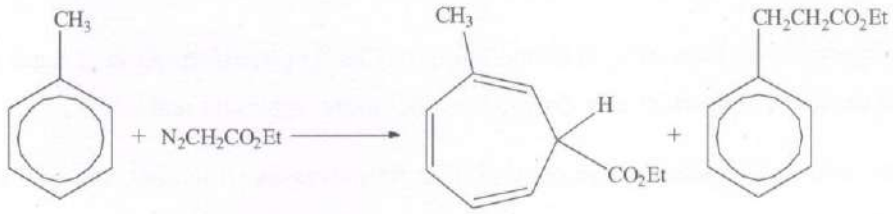
12. What happens when p-chlorotoluene is treated with $NaNH_2$ in liq. NH_3? 4

13. Carry out following SN^2 substitution reaction. 4



14. Draw the reaction-energy diagram for nitration of benzene. 4

15.



(A)

Mention the reactive intermediate involved in the formation of "A" and give mechanism. 4

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Section-II

This Section comprises *six* questions in three Groups. Answer *any four* questions taking *at least one* question from each Group.

Group-A

1. (a) Given a solution that is 0·5(M) in acetic acid. One litre of this solution is to be diluted to what extent in order to (i) double the pH? (ii) double the $[HO^-]$? (pk_a for acetic acid = 4·74) 5+5=10

   (b) Draw qualitative (approximate) MO energy-level diagram for NO. Is the molecule diamagnetic? What is the bond order in NO? 4+1+1=6

   (c) What is Bent's rule? Discuss with one suitable example. 3+2=5

   (d) What do you mean by a buffer solution? Discuss the mechanism of buffer action. 2+5=7

   (e) State Nernst equation defining each term in it. Discuss with an appropriate example how complex formation affects the redox potential of a redox couple. 2+6=8

   (f) Calculate the pH of an aqueous solution of 10^{-9}(M) HCl. 4

2. (a) What do you mean by crystal lattice energy of an ionic compound? What is Hess's law? In forming the crystal of MgO from Mg(S) and O_2(g), state the steps using Born Haber cycle to estimate the lattice energy of MgO (no numerical values or explanation needed). 2+2+5=9

   (b) 50 ml of 0·1(M) NaCl is titrated with 0·1(M) $AgNO_3$. Calculate the chloride ion concentration during titration (i) when no $AgNO_3$ was added, (ii) after addition of 10 ml $AgNO_3$ and (iii) after addition of 49·9 ml $AgNO_3$. 2+2+2=6

   (c) What is phosphazene? Write down the structure of tetracyclophosphazene. 1+3=4

   (d) Borazine is wrongly called as 'inorganic benzene'. Justify. 6

   (e) For 'particle in an one-dimensional box', state the differential equation for the wave function ψ. What should be the potential energy of the particle outside and inside the box? 2+1+1=4

   (f) Alkaline hydrolysis of CH_3I results in CH_3OH but CF_3I produces CF_3H. Explain. 4

   (g) An electron with charge 'e' and mass 'm' is moving in a circular orbit with average angular velocity ω. Find out the expression for its orbital magnetic moment given that the angular momentum of the electron is $\sqrt{l(l+1)}\frac{h}{2\pi}$ where l is the orbital angular momentum quantum number. 5

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(h) The ionic product of water at 95°C is 55 times of that at 25°C. A solution has pH 6·6 at 95°C. Is the solution acidic? Explain. 2

Group-B

3. (a) Coefficient of viscosity of a liquid is often determined by Ostwald viscometry. However, the principal equation in this connection is Poiseuille's equation: $\eta = \pi\Delta pr^4t/8lv$

Where η, Δp, r, l, t and v represent respectively coefficient of viscosity (η), pressure difference (Δp) resulting in the flow of the liquid through the capillary, radius (r) of the capillary, length (l) of the capillary and time (t) required for the flow of a definite volume (v) of liquid.
Relate all these terms with the ones considered during ostwald viscometric experiment. 8

(b) NaCl and KCl crystallizes in the same cubic fashion. However, X-ray diffraction (XRD) study reveals NaCl crystal to be FCC (face centred cubic) and KCl crystal to be SCC (simple cubic crystal). How would you rationalize it. 8

(c) When iodine is partitioned between water and benzene it is observed that the intensity of color in benzene layer is much draker than that in aqueous layer. With the addition of little amount of solid Kl, color of the benzene layer becomes appreciably fade. Justify the phenomenon. Which principle is applied here? 7

(d) In an experiment for determination of surface tension of water by capillary rise method the rise of water in the capillary is found to be 2 cm. If I cut the tube in the middle of it what will happen? 7

(e) $NH_3 + HCl \rightleftharpoons NH_4Cl$
At room or low temperature the forward reaction is spontaneous but at higher temperature the backward reaction is spontaneous — Rationalize from thermodynamic point of view. 10

4. (a) Among the postulates of kinetic theory of gases which two are grossly incorrect for real gases? How have these two issues been taken care of by van der Waals? 2+7=9

(b) Describe the origin of surface tension on a liquid-air interface. Using Langmuir-Blodgett trough (often called Langmuir balance) how can one determine the cross sectional area of a soap molecule? 3+6=9

(c) Among simple cubic crystal (SCC), face centered cubic crystal (FCC) and body centered cubic crystal (BCC) which one is most compact? Establish the order of their relative compactness. 2+8=10

(d) Can an endothermic reaction be spontaneous? Justify your response from thermodynamic point of view. 1+6=7

(e) Give a simple example of an endothermic process. How can one make the process to move in the forward direction more efficiently? 2+3=5

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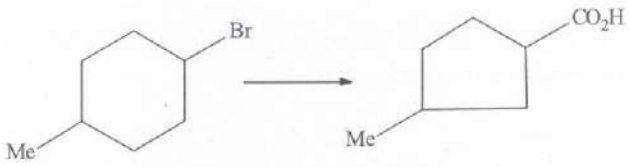
Group-C

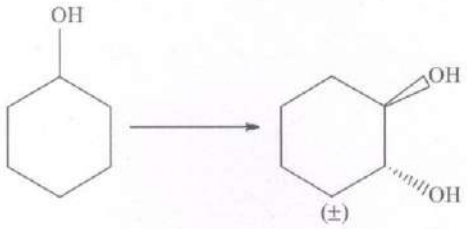
5. (a) The mass spectra two alkyl benzene of molecular formula $C_{10}H_{14}$ show following peaks:

Compound A → B. P. at m/e 91

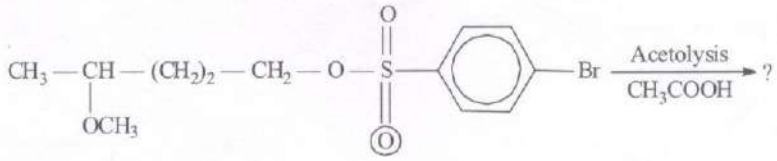
Compound B → B. P. at m/e 105 and a weak peak at m/e 91. Establish the structure of A and B. 5

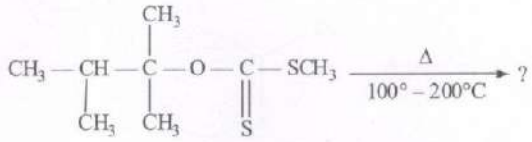
(b) Carry out following transformation with mechanism. 5+5=10

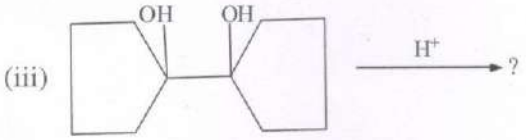
(i) 

(ii) 

(c) Write the products of the following reaction with mechanism. 5+5+5+5+5=25

(i) 

(ii) 

(iii) 

(iv) 

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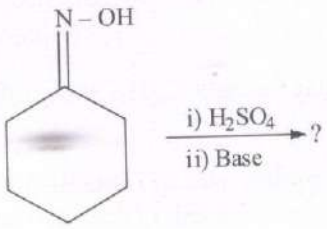
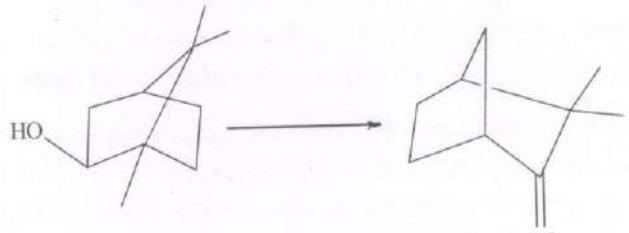
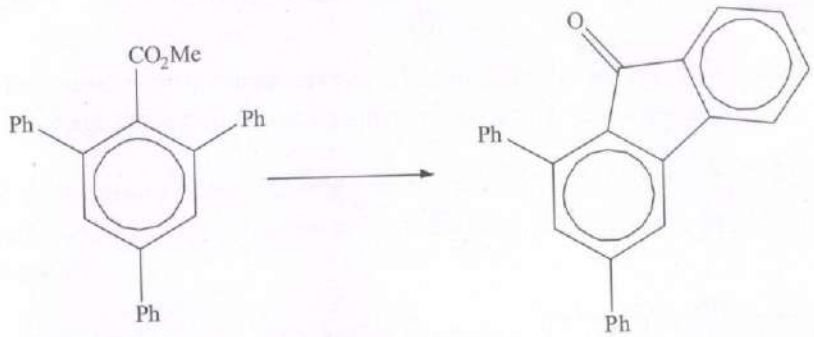
(v) 

6. (a) Carry out following conversion with mechanism. 5+5+5+5=20

(i) 

(ii) PhCHO ⟶ PhCDO

(iii) PhCHO ⟶ 

(iv) 

(b) Explain order of solvolysis of the following compounds. 10

(i) $CH_2 = CH - CH_2Cl$, (ii) Ph CH_2Cl (iii) $MeOCH_2Cl$

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(c) When acetone is treated with a base, a liquid compound is formed with b.p. 130°C. Its spectral data are as follows:

UV: λ_{max} 238 nm ε 11700

1R: 1600 cm^{-1}(m), 1595 cm^{-1}(s)

^{1}HNMR: δ 2·1 (6H, s), 6·15(1H, s)

Mass m/e: 55(100), 83(90), 43(78), 98(49), 29(46), 39(43), 27(42), 53(13), 41(13), 28(8).

Deduce the structure of the compound and account for all the observed spectral data. 10

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